DATA VALIDATION PLAN (Volume 1 of 2)

Sauget Area 1
Support Sampling Project

Solutia, Inc.
St. Louis, Missouri

February 2000

O'BRIEN & GERE
ENGINEERS, INC.

Data Validation Plan

Solutia Area 1 Support Sampling Project

Solutia, Inc.
St. Louis, Missouri

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March 16, 2000

Mr. Michael McAteer
U. S. EPA - Region 5
77 West Jackson Boulevard (SR-6J)
Chicago, Illinois 60604-3590

Re: Sauget Sites Area I January 21, 1999 Administrative Order by Consent
- Replacement Data Validation Plan

Dear Mr. McAteer,

Pursuant to the January 21, 1999 Administrative Order By Consent for the Sauget Area I Site, Sauget and Cahokia, Illinois, Section XVI Modifications, Solutia Inc. ("Solutia") requests permission to replace the Data Validation Plan prepared by Environmental Standards, Inc. ("ESI"), identified as Volume 4 of the approved September 9, 1999 Support Sampling Plan, with the enclosed February 2000 Data Validation Plan, Volumes I and II, prepared by O'Brien & Gere ("OBG").

Solutia has been unable to reach agreement with ESI on the scope and cost of data validation, management and mapping for Sauget Area I Support Sampling Plan. As a result of these disagreements, Solutia solicited competitive bids from ENSR, ESI, OBG, and ROUX, Inc. Based on the quality of their proposal, experience of their team and competitive price - data validation, management and mapping was awarded to OBG.

Solutia believes there are no substantial differences between the two plans. If any discrepancies are found with the OBG plan, it will be corrected immediately to reflect the data validation approach included in the original approved ESI plan.

Sincerely,

D. M. Light
Manager, Remedial Projects
Sauget Sites Area I Project Coordinator

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1. Introduction

This Data Validation Plan includes the Data Validation Standard Operating Procedures (SOPs) which have been developed by O'Brien & Gere Engineers, Inc. (O'Brien & Gere) on behalf of Solutia, Inc. (Solutia). The SOPs will be used by the O'Brien & Gere Engineers Data Validation team for partial and full validation (referred to as Level III and Level IV, respectively), for the Solutia Sauget Area 1 Project. The SOPs, which will be used as worksheets that will be completed by the O'Brien & Gere validators, present the data validation approach that will be used to evaluate samples analyzed by the following United States Environmental Protection Agency (USEPA) methods:

- Volatile organics by 8260B and TO-17
- Semivolatile organics by 8270C and TO-13
- Pesticides by 8081A
- Polychlorinated biphenyls (PCBs) by 608 and TO-4
- Herbicides by 8151A
- Total Petroleum Hydrocarbons (TPH) by 8015B
- Dioxin/Dibenzofurans by 8280A, 8290, and TO-9
- Metals by 6010B
- Mercury by 7470A and 7471A
- Cyanide by 9010
- Copper by 7211
- Zinc by 7951

The SOPs are based on the following documents (where applicable):

- U.S. Environmental Protection Agency (USEPA). Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois.

- U.S. Environmental Protection Agency (USEPA). Region V. 1993. *Standard Operating Procedure for Validation of CLP Inorganic Data*, Chicago, Illinois.

- U.S. Environmental Protection Agency (USEPA). 1994. *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.

- U.S. Environmental Protection Agency (USEPA). 1994. *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*, EPA-540/R-94/013. Washington D.C.

- U.S. Environmental Protection Agency (USEPA). 1994. *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)*, New York.

- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

- U.S. Environmental Protection Agency (USEPA). 1988. *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-4, Method for the Determination of Organochlorine Pesticides and Polychlorinated Biphenyls In Ambient Air,* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.

- U.S. Environmental Protection Agency (USEPA). 1999. *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-9A Determination of Polychorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans In Ambient Air,* Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.

- U.S. Environmental Protection Agency (USEPA). 1985. *Determination of Pesticides and PCBs in Water and Soil/Sediment by GC/MS*, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio.

In the development of the O'Brien & Gere SOPs, the following hierarchy was used in the use of guidance documents. USEPA Region V data validation guidelines were used as guidance in developing the SOPs for volatile organics, semivolatile organics, pesticides, PCBs, herbicides, metals, mercury, cyanide, copper, zinc, and TPH. USEPA Region II data validation guidelines were used as guidance in developing the SOPs for dioxin since Region V guidelines were not available for the dioxin/dibenzofuran methodologies. Since the USEPA Region V data validation guidelines were intended to be applied to samples analyzed using Contract Laboratory Program (CLP) methodologies, the method criteria presented in the validation guidelines have been modified to reflect the specific method requirements used in this project. The same approach that the USEPA Region V guidelines uses in the application of qualifiers to sample results when excursions from the method criteria are detected has been used in these SOPs. In the case that USEPA Region V

guidelines deferred to the USEPA National Functional Guidelines, or the USEPA Region V guidelines did not address a method parameter, the SOPs reflect the USEPA National Functional Guidelines approach to data validation. In many of the SOPs, method information was added for use by the data validation team in evaluating the sample data.

The following quality assurance/quality control (QA/QC) parameters will be evaluated during the full validation process-

Analyses for volatile organics and semivolatile organics (where applicable):

1. Holding times, sample preservation, and percent solids
2. Dilutions
3. GC/MS tuning criteria
4. Initial and continuing calibration
5. Blank analysis
6. Surrogate recovery
7. MS/MSD analysis
8. Field duplicate analysis
9. LCS analysis
10. Internal standards performance
11. Compound identification and quantitation and system performance
12. Reported detection limits
13. System performance
14. Data completeness

Analyses for pesticides, TPH, and herbicides (where applicable):

1. Holding times, sample preservation, and percent solids
2. Dilutions
3. GC performance
4. Analytical sequence
5. Initial calibration and calibration verification
6. Blank analysis
7. Surrogate recovery
8. MS/MSD analysis
9. Field duplicate analysis
10. LCS analysis
11. Retention time windows
12. Compound identification, quantitation, and reported detection limits
13. Cleanup verification
14. Confirmation analysis
15. System performance
16. Data completeness

Analysis for metals, mercury and cyanide (where applicable):

1. Holding times, sample preservation, and percent solids
2. Initial and continuing calibration
3. Blank analysis
4. ICP interference check sample analysis

5. MS/MSD analysis
6. Field duplicate analysis
7. LCS analysis
8. Laboratory duplicate analysis
9. ICP serial dilution analysis
10. Furnace atomic absorption analysis
11. Verification of instrument parameters
12. Instrument detection limits
13. Linear ranges
14. Analyte quantitation, and reported detection limits
15. Method of standard additionsData completeness

Analysis for PCBs, dioxin/dibenzofurans analyses (where applicable):

1. Holding times, sample preservation, and percent solids
2. Instrument performance (mass calibration, GC column performance check)
3. Initial and continuing calibration
4. Blank analysis
5. Internal standard criteria
6. Recovery standard criteria
7. Duplicate analysis
8. MS/MSD analysis
9. Field duplicate analysis
10. Sample data (identification)
11. Estimated detection limits
12. Estimated maximum possible concentration (EMPC)
13. Second column confirmation
14. Sample reanalysis
15. Toxicity equivalency factor (TEF)
16. Data completeness

For partial validation, the following parameters will be evaluated-

Analyses for volatile organics and semivolatile organics:

1. Holding times, sample preservation, and percent solids
2. Surrogate recovery
3. MS/MSD analysis
4. Field duplicate analysis
5. LCS analysis
6. Internal standards performance

Analyses for pesticides, TPHs, and herbicides

1. Holding times, sample preservation, and percent solids
2. Blank analysis
3. Surrogate recovery
4. MS/MSD analysis
5. Field duplicate analysis
6. LCS analysis

Analysis for metal, mercury and cyanide (where applicable):

1. Holding times, sample preservation, and percent solids
2. Blank analysis
3. ICP interference check sample analysis
4. Spike analysis
5. Field duplicate analysis
6. LCS analysis
7. Laboratory duplicate analysis
8. ICP serial dilution analysis

Analysis for PCBs, dioxin/dibenzofuran analyses (where applicable):

1. Holding times, sample preservation, and percent solids
2. Blank analysis
3. Surrogate recovery
4. Internal standard criteria
5. Recovery standard criteria
6. MS/MSD and duplicate analysis
7. LCS analysis
8. Field duplicate analysis

For this project, approximately 10% of the sample data, per matrix, will undergo full (Level IV) validation. This process, as demonstrated in the SOPs, will involve complete review of the data packages for each parameter, as listed above. Approximately 10% of the sample calculations and identifications will be checked during the full validation using the raw data provided in the data packages.

For partial validation (Level III), the validation team will only evaluate information provided by the laboratory in summary form. Raw data will not be evaluated. If, however, a serious issue is detected through the validation process, additional evaluation may be performed by the validation team for these data packages, if requested by the Solutia Project Manager.

When performing the data validation, the Corrective Action tables and the detection limits presented in the project specific Quality Assurance Project Plan (QAPP) will be used as guidance and will take precedence when discrepancies are detected between the method requirements and the QAPP. A copy of the QAPP will be available to the validation team during the validation process.

During the validation process, the worksheets will be completed by the validation team. After the validation is completed, the validation worksheets will be utilized to generate the validation report and will then be stored in the project file for reference.

If, during the validation process, a serious method requirement excursion that will affect data quality is detected, the O'Brien & Gere Data Validation team will contact the laboratory and Solutia to discuss the issue, its severity, and corrective action that may be implemented.

If discrepancies between the raw data provided in the data packages and the summary forms are detected, a more in-depth and comprehensive review of the data will be performed. These discrepancies could include transcription errors and calculation errors. The laboratory will be contacted to provide explanations and corrections. If the discrepancies will affect data generation and quality, the Solutia Project Manager will be contacted.

The data validation report will be generated based on the information documented on the worksheets. The report will consist of the following: qualified sample results, data review narrative with discussion of excursions that resulted in qualified of sample results, methods used, data qualifier definitions, cross reference table listing the samples analyzed, dates collected, types of methods utilized, laboratory identification and client identification and matrix.

Table 1 presents the number of samples, the sample matrices, and the methods involved in this project.

Table 1 - Number of Samples to be Validated For Sauget Area 1 Support Project

Matrix	VOCs	SVOCs	PCBs	Pesticides	Herbicides	Dioxin	Metals	Hg
Waste	Method 8260B	Method 8270C	Method 680	Method 8081A	Method 8151A	Method 8280A Method 8290	Method 6010B	Method 7471A
Level III	30	28	28	28	28	28	28	28
Level IV	3	3	3	3	3	3	3	3
Sediment	Method 8260B	Method 8270C	Method 680	Method 8081A	Method 8151A	Method 8280A Method 8290	Method 6010B	Method 7471A
Level III	25	23	146	23	23	23	23	23
Level IV	3	3	17	3	3	3	3	3
Soil	Method 8260B	Method 8270C	Method 680	Method 8081A	Method 8151A	Method 8280A Method 8290	Method 6010B	Method 7471A
Level III	178	155	155	155	155	94	155	155
Level IV	20	18	18	18	18	11	18	18
Surface Water	Method 8260B	Method 8270C	Method 680	Method 8081A	Method 8151A	Method 8280A Method 8290	Method 6010B	Method 7470A
Level III	25	23	23	23	23	23	23	23
Level IV	3	3	3	3	3	3	3	3
Ground Water	Method 8260B	Method 8270C	Method 680	Method 8081A	Method 8151A	Method 8280A Method 8290	Method 6010B	Method 7470A
Level III	232	170	170	170	170	82	170	170
Level IV	26	19	19	19	19	10	19	19
Air	Method TO-17	Method TO-13	Method TO-4	NA	NA	Method TO-9	Method 6010B	Method 7470A
Level III	17	15	15	0	0	15	15	15
Level IV	2	2	2	0	0	2	2	2
Fish Fillets	NA	Method 8270C	Method 680	Method 8081A	Method 8151A	Method 8280A Method 8290	Method 6010B	Method 7471A
Level III	0	9	9	9	9	9	9	9
Level IV	0	1	1	1	1	1	1	1
Subtotals								
Level III	507	423	546	408	408	274	423	423
Level IV	57	49	63	47	47	33	49	49
TOTALS	564	472	609	455	455	307	472	472

Section 1

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8260B Volatile Organics – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8260B Volatile Organics – Partial Validation

O'Brien & Gere Engineers Data Validation Form - USEPA Method 8260B Volatile Organics
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____ Trip Blanks:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ FULL VALIDATION
Method reference: USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*. 3rd Edition. Washington, D.C.

CT	Sample, TB, EB, MS/MSD, FD Identification	Date collected 1999 2000	Date received 1999 2000	Method 5030B 5035 8260B	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number
MS/MSD indicates matrix spike/matrix spike duplicate

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
For Analyses of Volatile Organics by USEPA SW-846 Method 8260B

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*. Chicago, Illinois
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington. D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8260B. (National Functional Guidelines and Region V guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

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Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 List below any volatile samples that were received with headspace or air bubbles?
ACTION: If both VOA vials for a sample have air bubbles or the VOA vial analyzed had air bubbles, flag all positive results "J" and all non-detects "R".
Action: Use professional judgement. Generally if significant headspace is present, reject associated sample results and detection limits. Notify the Project QA/QC Officer that the affected samples must be resampled and reanalyzed.

1.4 Were the correct units indicated, µg/L for waters and µg/kg for soils?

1.5 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).
ACTION: For 8260 – the smallest soil size permitted is 0.5g. If any soil sample is smaller than 0.5g, document in the Data Assessment.

1.6 Were raw data to support analyses and QC operations present and complete?

Actions: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.7 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then flag all positive results with a "J" and all non-detects "UJ".

1.8 Were any of the samples diluted? Were dilutions performed when necessary? Note if samples were combined due to dilutions.

1.9 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.10 Were trip blanks, equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8260B: Aqueous samples analyzed within 7 days or 14 days for preserved water samples (cooled (@ 4 C) samples; soil/sediment samples 14 days (cooled (@ 4 C).

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

Note: For Encore samplers for soil; samples must be analyzed within 48 hours; otherwise samples must be transferred from Encore samplers and analyzed within 14 days from collection.

VALIDATION ACTIONS:

a. If holding times are exceeded associated sample results are flagged as estimated (UJ, J).
b. If correct preservation was not used, associated sample results are flagged as estimated (UJ, J).
c. If holding times are grossly exceeded (more than twice the requirements) for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected, R.

2.2 Summarize below the samples qualified for holding time excursions.

Sample ID (Client/lab)	Date Collected	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogate compounds prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the purge and trap gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries.
The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured (if the dilution is ≥ 5). If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.
For method 8260 – toluene-d8, 4-bromoflurobenzene, 1,2-dichloroethane-d4, dibromofluoromethane - 50-250 ng or lower for more sensitive instruments for water or low level soils)

Any time there are two or more analyses for a particular sample, the reviewer must determine which are the best data to report. Considerations should include but are not limited to:
a. System monitoring compound recovery (marginal versus gross deviation).
b. Technical holding times.
c. Comparison of the values of the target compounds reported in each sample analysis.
d. Other QC information, such as performance of internal standards.

50μg/L = 50ng/ml * 5 ml = 250 ng
Percent recovery = conc found/conc spiked * 100

VALIDATION ACTIONS: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).

b. If %recovery is 10%-upper control limit, flag associated sample results and detection limits as estimated (UJ,J).

c. If %recovery is > upper control limit, flag **positive** results as estimated (J).

d. If surrogates not used or not evaluated contact laboratory for explanation and describe problems/resolutions in final narrative report. Alert Project Manager immediately.

e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.

f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data.

g. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.3 List below samples qualified for surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:
TD8 – toluene-d8
4BFB - 4-bromofluorobenzene
12DCE – 1,2-dichloroethane-d4
DBFM – dibromofluoromethane

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs then evaluated

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)? If samples are extracted, one MS per extraction batch.)
4.2 Were laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

For 8260 – At a minimum, the target compounds 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, benzene are used. The MS solution should contain the compounds that are expected to be in the samples. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 10 to 50 times the MDL, 20 times the quantitation limit, or mid calibration range. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.
Validation Actions: Qualification is limited to the unspiked sample only.

RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are approximated (J).

b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.

c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).

c. If RPD criteria are not met, approximate **detected** results (J) and non detected results approximate (UJ).

d. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

e. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.4 List all MS/MSDs and list below samples qualified for MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limits]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for Laboratory Control Samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. The LCS must be extracted and analyzed concurrently with the samples in the batch, using the same instrumentation as the samples. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

For 8260 – The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 10 to 50 times the MDL, 20 times the quantitation limit, or mid calibration range. Until lab control limits are generated, 70-130% is used to evaluate LCS recoveries. In-house limits should fall within these limits. Otherwise, compare the recoveries to lab generated control limits.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).

b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).

c. If LCS recoveries <10%, reject detection limits R, approximate detected results (J).

d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List below LCSs and samples qualified for LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client/lab ID)

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, trip blanks, and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.
A method blank is analyzed for 8260 analysis to ensure that the total system (introduction device, transfer lines, storage, and GC/MS system) is free of contamination.

Note: B flags applied by the lab should not be removed from Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Inform PM immediately. Alternatively, field and or trip blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment/Trip Blanks/ Storage Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

6.2.2 Were trip blanks shipped with each sample cooler containing samples for volatile analyses?

Validation Actions: If no, note in data report that an evaluation of field or shipping contamination could not be made with reference to specific sampling event.

6.2.3 Were storage blanks analyzed? Storage blanks are evaluated based on results from method blanks.

6.3 Were tentatively identified compounds reported? Were they detected in any of the blanks analyzed? TIC results are treated in the same manner as the target compounds in blanks.

6.4 There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, he/she should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. In this case, the "5x" or "10x" rules may not apply; the target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

6.5 If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as unusable (R) due to interference. This should be noted for action if the contamination is suspected of having an effect on the sample results.

6.6 If inordinate numbers of other target compounds are found at low levels in the blank(s), it may be indicative of a problem and should be noted for action.

6.7 Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected. The target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

Validation Action: Action levels are calculated at 5x the blank value and 10x for methylene chloride, acetone, 2-butanone. Blank samples **are not** to be qualified with respect to other blanks, with the exception of storage blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the data validation report.

If the sample concentration is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.8 List all blanks and any samples qualified due to blank contamination.
Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank ID	Compound	Concentration.	Action Level	Samples Affected (client/lab ID)

7.0 GC/MS TUNING CRITERIA

Tuning and performance criteria are established to verify GC/MS performance; to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.
Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is performed using a single scan no more than 20 scans prior to the elution of BFB (not part of the BFB peak). Other documented approaches suggested by the instrument manufacturer may be used. The following table provides criteria to follow. Otherwise, other tuning criteria may be used if method performance is not adversely affected. The samples, standards and associated QC samples must be analyzed using the same tune conditions, within the 12 hour clock that is started at the time of injection of the BFB solution.

7.1 Were GC/MS tuning performances for 50-ng injection of BFB analyzed for every twelve hours of sample analysis for each GC/MS instrument used?

7.2 Have the ion abundance criteria documented by the method been met for each tune (verify that ion abundance's have been normalized to m/z 95)?

7.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

7.4 Are the spectra of the mass calibration acceptable?

7.5 Was the tune performance standard injected at the beginning of the analytical sequence and were all the samples analyzed within the 12-hour clock?

VALIDATION ACTIONS:

a. If tuning has not been done, reject (R) associated sample data and contact laboratory for explanation. Discuss in data completeness section in the data validation report.
b. If no for 7.2, 7.4, or 7.5 reject associated sample results.
c. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described above, then additional information on the instrument performance checks should be obtained. If the techniques employed are found to be at variance with the method, the performance and procedures of the laboratory may merit evaluation. If the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than the BFB peak), then this should be noted for action.

The critical ion abundances are m/z 95/96, 174/175, 174/176, 176/177. Less important are relative abundances of 50 and 75.

4-Bromofluorobenzene Ions and Abundance Criteria for 8260B	
Mass	Ion Abundance Criteria
50	15-40 percent of the base peak
75	30-60 percent of the base peak
95	base peak, 100 percent relative abundance
96	5-9 percent of the base peak
173	less than 2 percent of mass 174
174	greater than 50 percent of the base peak
175	5-9 percent of mass 174
176	greater than 95 percent but less than 101 percent of mass 174
177	5-9 percent of mass 176

7.5 List all tunes and any samples qualified due to tune excursions

INSTRUMENT ID:

Unique Tune ID (Date/Time)	Comments	Tune Met	Heated Purge?	Samples Affected (client/lab ID)

8.0 GC/MS INITIAL CALIBRATION

Calibration criteria has been established to verify that GC/MS is capable of producing acceptable quantitative data. Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the target compound list. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.
All target compounds must have corresponding initial and continuing calibrations.

For 8260, internal calibration is used. Aqueous and soil samples may be purged at elevated temperatures as long as all standards, samples and QC samples are purged at the same temperature, appropriate trapping material is used, and the lab demonstrates acceptable method performance. A minimum of five concentrations of standards, prepared in organic-free water, **with one concentration being at or below the project DQO (establishing the method quantitation limit – which must be as low as the regulatory or action limit)** and the remaining concentrations should correspond to the expected range of sample concentrations and should not be greater than the working range of the detector. The calibration curve is developed using the volume of samples that will be analyzed. Use internal standards fluorobenzene, chlorobenzene-d5, 1,4-dichlorobenzne-d4 or other compounds that have similar retention times at 50 µg/L or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.3 relative to the internal standards. Area is used to calculate response factors. The internal standard used for calculation should have a retention time closest to the analyte.

RF = Comp response *IS concentration/IS response * Comp conc

The system performance check compounds (SPCCs), which are evaluated for compound stability and degradation caused by contaminated lines or active sites in the system, must meet mean response factor criteria: chloromethane RF-0.10, 1,1-dichloroethane RF-0.10, bromoform RF-0.10, chlorobenzene RF-0.30, and 1,1,2,2-tetrachloroethane RF-0.30.

The calibration check compounds (CCCs) , which are evaluated for integrity of the system; high variability may indicate system leaks or reactive sites on the column, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, vinyl chloride, must be equal to or less than 30%.

The retention time should agree within 0.06 relative retention time units in each calibration standard.

Linearity – Both linear and nonlinear calibration is allowed. Nonlinear calibration may be necessary for low detection limits.

Linear calibration using average calibration or RF – calibration factors and RFs are a measure of the slope of the calibration relationship and assumes the curve passes through the origin. The factor should not vary with the concentration of the standard. However, when the variation, measured as the relative standard deviation (RSD) is less than or equal to 15%, the use of the linear model is appropriate and the average calibration or RF is used for concentration.
If the RSD of target analytes is greater than 15%, the initial calibration may be acceptable is the mean of the RSDs for all analytes is less than or equal to 15%. This approach will lead to greater uncertainty for those analytes for which the RSD is greater than 15%.

Linear calibration using least squares regression – If the RSD is greater than 15%, or if the analyst so chooses, linearity through the origin cannot be assumed and a linear regression of response verses concentration equation that does not pass through the origin may be used. The instrument response is dependent variable (y) and the concentration is the independent variable (x). The regression will produce the slope and intercept for a linear equation (y=mx+b) where y is the peak area, m is the slope, x is the concentration and b is the intercept. The origin is not forced through zero and do not use the origin as the sixth calibration point. The regression calculation will result in the correlation coefficent – r –, which is a measure of the "goodness of fit". A value of 1.00 is perfect, and for quantitative purposes, r must be greater than or equal to 0.99.

Non-linear calibration – if other approaches don't meet criteria, no more than third order non-linear may be used. First order (linear) requires five standards, second order (quadratic) model requires six standards and third order requires seven standards. The "goodness of fit" of the polynomial equation is evaluated by the weighted coefficient of the determination (COD), which must be greater than 0.99.

8.1 Were initial calibrations performed at the required concentrations prior to sample analysis, whenever GC/MS system is modified, and whenever continuing calibration criteria are exceeded?
Note: Initial and continuing calibrations for water analysis are also used to evaluate medium soil analysis. Verify that secondary ion quantitation has only been performed when there were sample interferences with the primary ion. If secondary ion quantitation has been performed the laboratory must document reasons in case narrative.

Validation Actions:
Check QAPP criteria for remaining compounds.

a. If initial calibration data can not provided, reject associated sample data (R).

b. If RRF <criteria (SPCC criteria, QAPP criteria for remaining analytes) reject sample detection limits (R), and approximate detected results (J) for the affected compounds.

c. If %RSD > criteria (CCC criteria and QAPP criteria for remaining analytes) approximate detected and non-detected results (UJ, J).

8.2 Check for transcription/calculation errors; check a minimum of one compound to verify that calibration factors and %RSDs have been calculated correctly using the internal standard. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Show calculations below.

Initial and continuing calibration criteria for USEPA Method 8260B aqueous and soil				
Primary Ion ***Internal standard** **SPCC (S)** **CCC (C)**	**Analyte**	**Minimum RRF**	**Maximum %RSD**	**Maximum % Difference**
50, 1, S	chloromethane	0.10	50	50
94, 1	bromomethane	0.05	50	50
62, 1, C	vinyl chloride	0.05	30	20
64, 1	chloroethane	0.05	50	50
84, 1	methylene chloride	0.05	50	50
58, 1	acetone	0.01	50	50
76, 1	carbon disulfide	0.05	50	50
96, 1, C	1,1-dichloroethene	0.05	30	20
63, 1, S	1,1-dichloroethane	0.10	50	50
96, 1	1,2-dichloroethene (total)	0.05	50	50
83, 1, C	chloroform	0.05	30	20
62, 1	1,2-dichloroethane	0.05	50	50
65, 1	1,2-dichloroethane-d4	0.05	50	50
72, 1	2-butanone	0.01	50	50
97, 2	1,1,1-trichloroethane	0.05	50	50
117, 2	carbon tetrachloride	0.05	50	50
83, 2	bromodichloromethane	0.05	50	50
63, 2, C	1,2-dichloropropane	0.05	30	20
75, 2	cis-1,3-dichloropropene	0.05	50	50
95, 2	trichloroethene	0.05	50	50
129, 2	dibromochloromethane	0.05	50	50
83, 2	1,1,2-trichloroethane	0.05	50	50
78, 2	benzene	0.05	50	50
75, 2	trans-1,3-dichloropropene	0.05	50	50

Initial and continuing calibration criteria for USEPA Method 8260B aqueous and soil				
Primary Ion ***Internal standard** **SPCC (S)** **CCC (C)**	**Analyte**	**Minimum RRF**	**Maximum %RSD**	**Maximum % Difference**
173, 2, S	bromoform	0.10	50	50
43, 3	2-hexanone	0.01	50	50
100, 3	4-methyl-2-pentanone	0.01	50	50
164, 3	tetrachloroethene	0.05	50	50
83, 3, S	1,1,2,2-tetrachloroethane	0.3	50	50
92, 3, C	toluene	0.05	30	20
98, 3	toluene-d8	0.05	50	50
112, 3, S	chlorobenzene	0.3	50	50
91 3, C	ethylbenzene	0.05	30	20
104, 3	styrene	0.05	50	50
106, 3	xylenes (total)	0.05	50	50
95, 3	bromofluorobenzene	0.05	50	50

Note:
Internal standards are suggested; internal standards used must have retention times that are closest to the analytes:
1 – fluorobenzene
2 – chlorobenzene-d5
3 - 1,4-difluorobenzene

8.4 List below all initial calibrations and compounds qualified for initial calibration excursions.

INSTRUMENT ID:

Unique IC ID (Date)	Compound	RF [control limit] %RSD [control limits]	Action	Samples Affected (client/lab ID)

9.0 CONTINUING CALIBRATION/VERIFICATION

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Continuing calibration checks satisfactory performance of the instrument on a day-to-day basis. The initial calibration is verified once every 12 hours.

For 8260, a calibration standard near the midpoint concentration of the calibration range must meet the verification criteria.
The system performance check compounds (SPCCs), which are evaluated for compound stability and degradation caused by contaminated lines, poor standards, or active sites in the system, must meet mean response factor criteria: chloromethane RF-0.10, 1,1-dichloroethane RF-0.10, bromoform RF-0.10, chlorobenzene RF-0.30, and 1,1,2,2-tetrachloroethane RF-0.30.
The calibration check compounds (CCCs) , which are evaluated for integrity of the system; high variability may indicate system leaks or reactive sites on the column, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, vinyl chloride, must be equal to or less than 20% D, where %D is percent difference when performing the average response factor calibration and percent drift when using a regression calibration. Corrective action must be taken if these criteria are not met prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project, and not included in the standards, all analytes must meet the 20% D criterion.

The retention time of the internal standards must not change by more than 30 seconds from that in the mid-point standard of the most recent initial calibration sequence. Otherwise, corrections must be made and the samples analyzed under this calibration must be reanalyzed. The area of the internal standards must not change by a factor of two (-50% to +100%) from that in the mid-point standard of the most recent initial calibration sequence. Otherwise corrections must be made and the samples analyzed under this calibration must be reanalyzed.

9.1 Were continuing calibration standards analyzed for each twelve hours of sample analysis, for each analyte, for each GC/MS?

9.2 Was the continuing calibration standard compared to the correct initial calibration?

VALIDATION ACTIONS:

a. If no, contact laboratory for explanation and review in data completeness section. Reject associated sample data if continuing calibration data can not be provided (R).
b. If RRF <criteria (SPCC, QAPP criteria for remaining analytes) reject, (R) sample detection limits and approximate (J) detected results for the affected compounds.
c. If %D > criteria (CCC, QAPP criteria for remaining analytes) approximate detected and non-detected sample results (UJ,J).

9.3 Check for transcription/calculation errors; check a minimum of one compound to verify that calibration factors and %D have been calculated correctly using the specified internal standard. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Show calculation below.

9.4 List below all continuing calibrations, and samples qualified due to continuing calibration excursions.

INSTRUMENT ID:

Unique CC ID (Date)	Compound	RRF [control limit] %D [control limit]	Action	Samples Affected (client/lab ID)

11.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

11.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate ID	Compound	RPD

12.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION, AND SYSTEM PERFORMANCE

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present). The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand represent an absence of data and are, therefore, more difficult to assess. One example of detecting false negatives is the not reporting of a Target Compound that is reported as a TIC.
For quantitation evaluation, the objective is to ensure that the reported quantitation results and the detection limits are accurate.

For 8260, samples should be screened to minimize contamination of the instrument. Dilutions are performed to keep the analyte concentration in the upper half of the calibration range. Aliquots of less than 1 ml are not recommended. The qualitative identification of analytes is based on retention time, and on comparison of the sample mass spectrum to a reference mass spectrum generated by the lab using the conditions of the method.

1. The relative retention times (RRTs) must be within +0.06 RRT units of the standard RRT.
2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

a. The characteristic ions are the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum
b. The relative intensities of the characteristic ions must agree within + 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)
c. Structural isomers that produce similar mass spectra should be identified as individual isomers if they have different retention times. Resolution is achieved if the height of the valley between two peaks is less than 25% of the sum of the two peak heights.
d. Identification is hampered when sample components are not resolved and produce mass spectra containing ions contributed by more than one analyte. Appropriate selection of sample spectra and background spectra is important.
e. Examination of extracted ion current profiles can aid in the selection of spectra. When analytes coelute the identification may be met, but each spectrum will contain extraneous ions contributed by the coeluting compound.

12.1 Were the VOA reconstructed ion chromatograms, the mass spectra for the identified compounds, and the data system printouts included?
If no, contact laboratory and summarize problems and resolutions in data completeness section.

12.2 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other_____?
Actions: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement to qualify data.

12.3 Was the RRT of each reported compound within criteria?
RRT= RT analyte/RT internal standard

12.4 Did all the ions present in the mass spectrum meet criteria?
Note: If ions >10% in the sample spectrum are not present in the standard spectrum, verify that these have been accoutered for by the analyst.

12.5 Were sample and standard relative intensities within criteria?
Actions: If no for any of the above, use professional judgement to determine acceptability of data. If it is determined that incorrect identifications were made, all such data should be rejected (R) or changed to non-detected (U). Summarize qualifications performed below and in the narrative report.

12.6 Were samples reanalyzed at the appropriate dilution, when saturation occurred or when concentrations exceed linear range of the calibration curve?
Note: When sample dilution is performed, the laboratory typically reports two sets of sample data, diluted sample with responses within linear range and undiluted sample (least diluted sample is reported if two sets of dilutions were performed).
Action: Sample results quantitated with responses that exceed calibration range are approximated (UJ,J). In addition depending on data quality objectives of the project reanalysis of diluted extract may be required. Review resolutions in the narrative report.

12.7 Were correct quantitation ions, internal standard, calibration standard, and RF used?

12.8 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions and for soils, sample moisture?

ACTIONS: If no request resubmittal of data package.

Sample calculation:

Aqueous: Concentration (µg/L) = Area analyte * Conc IS * Dilution factor * Vol injected (µl) [purge = 1]
/Area IS*RF from IC *Volume sample purged (ml) * 1000

Low Soil: Concentration (µg/Kg) = Area analyte * Conc IS * Dilution factor * Vol injected (µl) [purge = 1]
/Area IS*RF from IC *weight sample (g) * 1000

Medium soil: Concentration (mg/Kg) = Area analyte * Conc IS * Dilution factor * Vol final extract [5000ul]
/Area IS*RF from IC *weight sample (g) * Vol extract analyzed (100ul)

12.9 Was the complete target compound list reported for each sample result?

12.10 Were compounds detected at concentrations below CRQL (or PQL) reported and qualified with a "J"?

ACTIONS: If no, request corrections from the laboratory. Summarize necessary corrections.

Document which sample analyses were reviewed and indicate frequency of raw data review. Approximately 10% of data should be verified through raw data review. Show calculations below.

13.0 TENTATIVELY IDENTIFIED COMPOUNDS (TICs)

Note: TICs may not be required for the project. If required for the project, non-target analytes of apparent greatest concentration may be tentatively identified via library search.

Chromatographic peaks in volatile analyses, including blanks, that are not target analytes, surrogates, or internal standards are potential tentatively identified compounds (TICs). TICs must be qualitatively identified via a forward search of the Spectral Library, and the identifications assessed by the data reviewer.

For each sample, the laboratory must conduct a mass spectral search of the library and report the possible identity for the appropriate number of the largest volatile fraction peaks which are not surrogates, internal standard, or target compounds, but which have area or height greater than the area or height of the nearest internal standard.

Guidelines for tentative identification are as follows:
a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.
b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.
c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target compounds.
f. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Library reductions can sometimes create these discrepancies.

The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.
Examples:
a. Common laboratory contaminants: CO (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 µg/L or 4000 µg/Kg.
b. Solvent preservatives such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.
c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

Occasionally, a target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.
TIC results which are not sufficiently above the level in the blank should not be reported.

13.1 Was library searching required for the project?
13.2 Were Tentatively Identified Compounds properly identified with scan number or retention time, estimated concentration?
13.3 Were the mass spectra for TICs and associated "best match" spectra included?
13.4 Were each of the ions present in the reference mass spectra with a relative intensity greater than 10% also present in the sample mass spectrum?
13.5 Did TIC and "best match" standard relative ion intensities agree within 20%?
13.6 Were TICs quantitated using the closest internal standard free of contamination and using a RRF of 1.0?

Use professional judgement to determine acceptability of TIC identifications. If it is determined that an incorrect identification was made, note below qualifications made to the sample data.

ACTIONS:

1. All TIC results should be qualified "NJ", tentatively identified, with approximated concentrations.
2. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.
3. If all peaks were not library searched and quantitated, these data are requested from the laboratory.
4. If errors are large, request resubmittal of data package.

13.7 Summarize TICs qualified as a result of TIC excursions if required.

Sample ID	TIC	Concentration	Action

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form - USEPA Method 8260B Volatile Organics
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____ Trip Blanks:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ PARTIAL VALIDATION
Method reference: USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*. 3rd Edition. Washington, D.C.

CT	Sample, TB, EB, MS/MSD, FD Identification	Date collected 1999 2000	Date received 1999 2000	Method 5030B 5035 8260B	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number
MS/MSD indicates matrix spike/matrix spike duplicate

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
For Analyses of Volatile Organics by USEPA SW-846 Method 8260B

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8260B. (National Functional Guidelines and Region V guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation raw data is not reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues regarding problems with sample receipt or condition of samples.

1.2 List below any volatile samples that were received with headspace or air bubbles.
ACTION: If both VOA vials for a sample have air bubbles or the VOA vial analyzed had air bubbles, flag all positive results "J" and all non-detects "R".
Action: Use professional judgement. Generally if significant headspace is present, reject associated sample results and detection limits. Notify the Project QA/QC Officer that the affected samples must be resampled and reanalyzed.

1.3 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).
ACTION: For 8260 – the smallest soil size permitted is 0.5g. If any soil sample is smaller than 0.5g, document in the Data Assessment.

1.4 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then flag all positive results with a "J" and all non-detects "UJ".

1.5 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.6 Were trip blanks, equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8260B: Aqueous samples analyzed within 7 days or 14 days for preserved water samples (cooled (@ 4 C) samples; soil/sediment samples 14 days (cooled (@ 4 C).

Note: For Encore samplers for soil; samples must be analyzed within 48 hours; otherwise samples must be transferred from Encore samplers and analyzed within 14 days from collection.

Validation Actions:

a. If holding times are exceeded associated sample results are flagged as estimated (UJ, J).
b. If correct preservation was not used, associated sample results are flagged as estimated (UJ, J).
c. If holding times are grossly exceeded (more than twice the requirements) for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected, R.

2.2 List below samples qualified for holding time excursions.

Sample ID (Client/lab)	Date Collected	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogate compounds prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the purge and trap gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries.
The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured (if the dilution is ≥ 5). If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.
For method 8260 – toluene-d8, 4-bromoflurobenzene, 1,2-dichloroethane-d4, dibromofluoromethane - 50-250 ng or lower for more sensitive instruments for water or low level soils)

Any time there are two or more analyses for a particular sample, the reviewer must determine which are the best data to report. Considerations should include but are not limited to:
a. System monitoring compound recovery (marginal versus gross deviation).
b. Technical holding times.
c. Comparison of the values of the target compounds reported in each sample analysis.
d. Other QC information, such as performance of internal standards.
Validation Actions: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).

b. If %recovery is 10%-upper control limit, flag associated sample results and detection limits as estimated (UJ,J).

c. If %recovery is > upper control limit, flag **positive** results as estimated (J).

d. If surrogates not used or not evaluated contact laboratory for explanation and describe problems/resolutions in final narrative report. Alert Project Manager immediately.

e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.

f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data.

g. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.2 List below samples qualified for surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:
TD8 – toluene-d8
4BFB - 4-bromofluorobenzene
12DCE – 1,2-dichloroethane-d4
DBFM – dibromofluoromethane

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs then evaluated

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)? If samples are extracted, one MS per extraction batch.)

4.2 Were laboratory batch QC performed?

For 8260 – At a minimum, the target compounds 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, benzene are used. The MS solution should contain the compounds that are expected to be in the samples. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 10 to 50 times the MDL, 20 times the quantitation limit, or mid calibration range. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.
Validation Actions: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are approximated (J).

b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.

c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).

c. If RPD criteria are not met, approximate **detected** results (J) and non detected results approximate (UJ).

d. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

e. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.3 List all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limits]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for Laboratory Control Samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. The LCS must be extracted and analyzed concurrently with the samples in the batch, using the same instrumentation as the samples. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

For 8260 – The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 10 to 50 times the MDL, 20 times the quantitation limit, or mid calibration range. Until lab control limits are generated, 70-130% is used to evaluate LCS recoveries. In-house limits should fall within these limits. Otherwise, compare the recoveries to lab generated control limits.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).

b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).

c. If LCS recoveries <10%, reject detection limits R, approximate detected results (J).

d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client/lab ID)

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, trip blanks, and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.
A method blank is analyzed for 8260 analysis to ensure that the total system (introduction device, transfer lines, storage, and GC/MS system) is free of contamination.

Note: B flags applied by the lab should not be removed from Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Inform PM immediately. Alternatively, field and or trip blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment/Trip Blanks/ Storage Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

6.4 Were trip blanks shipped with each sample cooler containing samples for volatile analyses?

Validation Actions: If no, note in data report that an evaluation of field or shipping contamination could not be made with reference to specific sampling event.

6.5 Were storage blanks analyzed? Storage blanks are evaluated based on results from method blanks.

6.6 If inordinate numbers of target compounds are found at low levels in the blank(s), it may be indicative of a problem and should be noted for action.

VALIDATION ACTION: Action levels are calculated at 5x the blank value and 10x for methylene chloride, acetone, 2-butanone. Blank samples **are not** to be qualified with respect to other blanks, with the exception of storage blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the data validation report.
If the sample concentration is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".

c. If the sample concentration is > Action level, qualification of data is not necessary.

6.7 List all blanks and any samples qualified due to blank contamination.
Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank ID	Compound	Concentration.	Action Level	Samples Affected (client/lab ID)

7.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity; (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

For 8260, Internal standards **may** be monitored in all samples, blanks, and standards. The QAPP should be consulted to determine if internal standard evaluation is required for the project. Use internal standards fluorobenzene, chlorobenzene-d5, 1,4-dichlorobenzne-d4 or other compounds that have similar retention times at 50 µg/L or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.3 relative to the internal standards. Area is used to calculate response factors. Use the internal standard used for calculation should have a retention time closest to the analyte.

7.1 Were internal standard areas of samples or blanks within +100% or -50% of the internal standard associated with the continuing calibration standard?

Note: The laboratory is required to reanalyze field, QC, and blank samples when internal standard criteria are not met.

VALIDATION ACTIONS:

a. If area count is above the limit, approximate (J) detected results for compounds quantitated with that internal standard.
b. If area count is below limits, approximate detected and nondetected results (UJ,J) for compounds quantitated with that internal standard.
c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R) and approximate detected results (J).

7.2 Are retention times of the internal standards within 30 seconds of the associated calibration standard?

VALIDATION ACTION:
If retention times are outside criteria, reject undetected results, R, for compounds quantitated with that internal standard. Be aware that false positive and negative results may exist so carefully examine chromatographic profile.

7.3 Were samples and method blanks reanalyzed when internal standard criteria was exceeded?

VALIDATION ACTION: Document in the narrative report that the laboratory was not in compliance with analytical method requirements.
If yes, and internal standard areas remain outside criteria, validate both sets of sample data with respect to above actions.

If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:
a. Magnitude and direction of the IS area shift.
b. Magnitude and direction of the IS retention time shift.
c. Technical holding times.
d. Comparison of the values of the target compounds reported in each fraction.
e. Other QC results.

7.4 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	Internal Standard	Internal Area and %R	Range (area)	Action

Note:
Fluorobenzene (FB) - chloromethane, bromomethane, vinyl chloride, chloroethane, methylene chloride, acetone, carbon disulfide, 1,1-dichloroethene, 1,1-dichloroethane, 1,2-dichloroethene (total), chloroform, 1,2-dichloroethane, 1,2-dichloroethane-d4, 2-butanone

Chlorobenzene-d5 (CBD5) - 1,1,1-trichloroethane, carbon tetrachloride, bromodichloromethane, 1,2-dichloropropane, cis-1,3-dichloropropene, trichloroethene, dibromochloromethane, 1,1,2-trichloroethane, benzene, trans-1,3-dichloropropene, bromoform

1,4-dichlorobenzene-d14 (DCB) - 2-hexanone, 4-methyl-2-pentanone, tetrachloroethene, 1,1,2,2-tetrachloroethane, toluene, toluene-d8, chlorobenzene, ethylbenzene, styrene, xylenes (total), bromofluorobenzene

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate ID	Compound	RPD

Section 2

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8270C Semivolatile Organics – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8270C Semivolatile Organics – Partial Validation

O'Brien & Gere Engineers Data Validation Form - USEPA Method 8270C Semivolatile Organics
Date:_____ **Number of samples and compounds per sample:**_____
Project Number:_____
Validator:_____ **Equipment Blanks:**_____
Project: _____ **Blind/Field Duplicates:**_____
Laboratory:_____ **MS/MSDs:**_____
QAPP:_____ **DV Guidelines: USEPA Region V**
Laboratory package number:_____ **FULL VALIDATION**
Method reference: USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*. 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8270C	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3510C 3550B 8270	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
For Analyses of Semivolatile Organics by USEPA SW-846 Method 8270C

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*. Chicago, Illinois
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8270C. (National Functional Guidelines and Region V guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR SEMIVOLATILE ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of semivolatile data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, µg/L for waters and µg/kg for soils?

1.4 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as approximate (J). If a soil sample other than TCLP contains more than 90% water, all data should be rejected (R).

1.5 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.6 Was appropriate clean-up used (GPC)?

1.7 Were any of the samples diluted? Were dilutions performed when necessary? Note if samples were combined due to dilutions.

1.8 Was raw data to support analyses and QC operations present and complete?

ACTIONS: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.9 List below any communication with laboratory regarding problems with data completeness, reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.10 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8270: Aqueous samples must be extracted within 7 days of collection and soil/sediment samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples must be stored at 4°C ±2.
Verify the collection and analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

VALIDATION ACTIONS:

a. If extraction holding times are exceeded, associated sample results are flagged as approximate (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as approximate (J) and non-detected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 List below samples qualified for holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates, prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries. The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

Surrogates are added such that 1 milliliter aliquot added to 1 liter of sample is equal to the concentration of 10 times the quantitation limit or near the mid-point of the calibration curve. If GPC is used, 2 milliliters are added to samples.
If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries cannot be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Any time there are two or more analyses for a particular fraction the reviewer must determine which are the best data to report. Considerations should include but are not limited to:
a. Surrogate recovery (marginal versus gross deviation).
b. Technical holding times.
c. Comparison of the values of the target compounds reported in each fraction.
d. Other QC information, such as performance of internal standards.

Percent recovery = (conc found/conc spiked)* 100
Semi-volatile surrogates are grouped as follows:

- Acid extractable: phenol-d6, 2-fluorophenol, and 2,4,6-tribromophenol.
- Base neutral: nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14.

VALIDATION ACTIONS: Qualification of data is necessary if two or more base-neutral or acid surrogates are out of control limits or if any one surrogate compound has a recovery <10%.

a. If %recovery is <10%, flag positive results as approximate (J) and reject detection limits, (R).
b. If %recovery is 10% to lower control limit, flag associated sample results and detection limits as approximate (UJ, J).
c. If %recovery is > upper control limit, flag **positive** results as approximate (J).
d. If one acid or base surrogate has a recovery >10%, but less than the lower limit and another acid or base has a recovery greater than the upper limit, flag positive results and detection limits as approximate (J, UJ).
e. If surrogates are not used, contact laboratory for explanation and describe problems/resolutions in final narrative report. Alert the Project Manager immediately.
f. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with method requirements.
g. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
h. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.3 List below samples qualified for surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:
PD6 - phenol-d6
2FP - 2-fluorophenol
246TP - 2,4,6-tribromophenol.
NB – nitrobenzene-d5
2FBP - 2-fluorobiphenyl
TP - terphenyl-d14

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate the effects of sample matrix on method performance. Representative compounds are spiked into a field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

For 8270 - At a minimum, the target compounds 1,2,4-trichlorobenzene, acenaphthene, 2,4-dinitrotoluene, pyrene, n-nitroso-di-n-propylamine, 1,4-dichlorobenzene, pentachlorophenol, phenol, 2-chlorophenol, 4-chloro-3-methylphenol, and 4-nitrophenol must be included in the spiking solutions. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. The concentration of the spike solution should be base/neutrals at 100 mg/L and acids at 200 mg/L for water and soil samples, and five times higher for waste samples. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.
RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and approximate non-detected results (UJ).
e. If complete fractions (acid/base) have recovery problems, all the target analytes in that fraction may be qualified if the MS did not contain all target analytes.
f. If MS/MSDs were not analyzed, contact the laboratory for an explanation and describe the problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
g. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.2 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for Laboratory Control Samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. The LCS must be extracted and analyzed concurrently with the samples in the batch, using the same instrumentation as the samples. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

For 8270 – The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If there are no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries are greater than control limits, approximate detected results (J).
b. If LCS recoveries are less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs were not analyzed, contact laboratory for explanation and describe the problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
e. If complete fractions (acid/base) have recovery problems, all the target analytes in that fraction may be qualified if the LCS did not contain all target analytes

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed for 8270 analysis to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contamination.

Note: B flags applied by the lab should not be removed from Form 1s.
6.1 Were method blanks analyzed for each group of samples of similar matrix?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination cannot be made. Alert the Project Manager immediately. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: Equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

6.3 Were tentatively identified compounds reported? Were they detected in any of the blanks analyzed? TIC results are treated in the same manner as the target compounds in blanks.

6.4 There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, he/she should qualify the data. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. In this case, the "5x" or "10x" rules may not apply; the target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

6.5 If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as rejected (R) due to interference. This should be noted for action if the contamination is suspected of having an effect on the sample results.

6.6 If inordinate numbers of other target compounds are found at low levels in the blank(s), it may be indicative of a problem and should be noted for action.

6.7 Instrument blanks should be analyzed after high concentrations, otherwise carryover may be suspected. The target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

Action levels are calculated at 5x blank (method) value (10x for phthalates). Blank samples **are not** to be qualified with

respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.
Instrument blanks should be analyzed after high concentrations, otherwise carryover may be suspected. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

VALIDATION ACTIONS:
Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the data validation report.
If the sample concentration (extract) is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".

b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration with a "U".

c. If the sample concentration is > Action level, qualification of data is not necessary.

6.8 Summarize all blanks and any samples qualified due to blank contamination.
Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 GC/MS TUNING CRITERIA

Tuning and performance criteria are established to verify GC/MS performance. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is performed using a single scan no more than 20 scans prior to the elution of DFTPP (not part of the DFTPP peak). Other documented approaches suggested by the instrument manufacturer may be used. The following table provides criteria to follow. Otherwise, other tuning criteria may be used if method performance is not adversely affected. The samples, standards and associated QC samples must be analyzed using the same tune conditions, within the 12 hour clock that is started at the time of injection of the DFTPP solution. For 8270, 50 ng/µL of decafluorotriphenylphosphine (DFTPP) is used. The standard should also contain ng/µL of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and PCP should not have peak tailing (<5%).

7.1 Were GC/MS tuning performances for 50-ng injection of DFTPP analyzed for every twelve hours of sample analysis for each GC/MS instrument used?

7.2 Have the ion abundance criteria documented by the method been met for each tune (verify that ion abundance's have been normalized to m/z 198)?

7.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

7.4 Are the spectra of the mass calibration acceptable?

7.5 Was the tune performance standard injected at the beginning of the analytical sequence and were all the samples analyzed within the 12-hour clock?

7.6 Did degradation of DDT and evaluation of benzidine and PCP meet criteria?

VALIDATION ACTIONS:

a. If tuning has not been done, reject associated sample data (R) and contact laboratory for explanation. Discuss in data completeness section in the data validation report.

b. If no for 7.2, 7.4, or 7.5 reject associated sample results (R).

c. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described above, then additional information on the instrument performance checks should be obtained. If the techniques employed are found to be at variance with the method, the performance and procedures of the laboratory may merit evaluation. If the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than the DFTPP peak), then this should be noted for action.

Some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/1990 and 442/443 are critical. These ratios are based on the natural abundances of carbon 12 and carbon 13 and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of the resolution adjustment and are very important. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. For instance, if m/z 275 has 40% relative abundance (criteria: 10.0-30.0%) and other criteria are met, then the deficiency is minor. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance for m/z 365 is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 0.75% minimum abundance criteria, the deficiency is not as serious.

Decafluorotriphenylphosphine Ions and Abundance Criteria for 8270C	
Mass	**Ion Abundance Criteria**
51	30-60 percent of 198
68	Less than 2 percent of 69
70	Less than 2 percent of 69
127	40 to 60% of 198
197	Less than 1 percent of 198
198	Base Peak, 100 percent relative abundance
199	5 to 9 percent of 198
275	10 to 30 percent of 198
365	Greater than 1 percent of 198
441	Present but less than 443
442	Greater than 40 percent of 198
443	17 to 23 percent of 442

7.5 List all tunes and any samples qualified due to tune excursions.

INSTRUMENT ID:

Unique Tune ID	Date/Time	Comments	Tune Met	Samples affected (client/lab ID) and action

8.0 GC/MS INITIAL CALIBRATION

Calibration criteria have been established to verify that GC/MS is capable of producing acceptable quantitative data. Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the target compound list. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.
All target compounds must have corresponding initial and continuing calibrations.

For 8270, internal calibration is used. Prepare a minimum of five concentrations of standards, **with one concentration being at or below the project DQO (establishing the method quantitation limit – which must be as low as the regulatory or action limit)** and the remaining concentrations should correspond to the expected range of sample concentrations and should not be greater than the working range of the detector. Use internal standards 1,4-dichlorobenzine-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12 or other compounds that have similar retention times at 40 ng/µg/L or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.2 relative to the internal standards. Area is used to calculate response factors. The internal standard used for calculation should have a retention time closest to the analyte.
RF = (Comp response *IS concentration)/(IS response * Comp conc)
The system performance check compounds (SPCCs), which are evaluated for compound stability and degradation caused by contaminated lines or active sites in the system, must meet mean response factor criteria of 0.05: n-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol.
The calibration check compounds (CCCs), which are evaluated for integrity of the system; high variability may indicate system leaks or reactive sites on the column, acenaphthene, 1,4-dichlorobenzene, hexachlorobutadiene, n-nitroso-diphenylamine, di-n-octyl phthalate, fluoranthene, benzo(a)pyrene, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2-nitrophenol, phenol, pentachlorophenol, 2,4,6-trichlorophenol, must be equal to or less than 30%.
The retention time should agree within 0.06 relative retention time units in each calibration standard.

Linearity – Both linear and nonlinear calibration is allowed. Nonlinear calibration may be necessary for low detection limits.

Linear calibration using average calibration or RF – calibration factors and RFs are a measure of the slope of the calibration relationship and assumes the curve passes through the origin. The factor should not vary with the concentration of the standard. However, when the variation, measured as the relative standard deviation (RSD) is less than or equal to 15%, the use of the linear model is appropriate and the average calibration or RF is used for concentration.
If the RSD of target analytes is greater than 15%, the initial calibration may be acceptable as the mean of the RSDs for all analytes less than or equal to 15%. This approach will lead to greater uncertainty for those analytes for which the RSD is greater than 15%.

Linear calibration using least squares regression – If the RSD is greater than 15%, or if the analyst so chooses, linearity through the origin cannot be assumed and a linear regression of response verses concentration equation that does not pass through the origin may be used. The instrument response is dependent variable (y) and the concentration is the independent variable (x). The regression will produce the slope and intercept for a linear equation (y=mx+b) where y is the peak area, m is the slope, x is the concentration and b is the intercept. The origin is not forced through zero and do not use the origin as the sixth calibration point. The regression calculation will result in the correlation coefficient – r –, which is a measure of the "goodness of fit". A value of 1.00 is perfect, and for quantitative purposes, r must be greater than or equal to 0.99.

Non-linear calibration – if other approaches don't meet criteria, no more than third order non-linear may be used. First order (linear) requires five standards, second order (quadratic) model requires six standards and third order requires seven standards. The "goodness of fit" of the polynomial equation is evaluated by the weighted coefficient of the determination (COD), which must be greater than 0.99.

8.1 Were initial calibrations performed at the required concentrations prior to sample analysis, whenever GC/MS system is modified, and whenever continuing calibration criteria are exceeded?
Verify that secondary ion quantitation has only been performed when there were sample interferences with the primary ion. If secondary ion quantitation has been performed the laboratory must document reasons in case narrative.

VALIDATION ACTIONS:
Check QAPP criteria for remaining compounds.

a. If initial calibration data cannot provided, reject associated sample data (R).

b. If RRF <criteria (SPCC, QAPP for remaining compounds) reject sample detection limits (R) and approximate detected results (J) for the affected compounds.

c. If RSD > criteria (CCC, QAPP for remaining compounds) approximate detected and non-detected results (UJ, J).

8.2 Check for transcription/calculation errors; check a minimum of one compound/internal standard to verify that calibration factors and %RSDs have been calculated correctly using the internal standard. Request corrections from the laboratory. Show calculation below.

Initial and continuing calibration criteria for USEPA Method 8270C aqueous and soil				
***Internal standard** **Primary ion** **SPCC (S)** **CCC (C)**	**Analyte**	**Minimum RRF**	**Maximum %RSD**	**Maximum % Difference**
1, 93	Bis(2-chloroethyl) ether	0.05	50	50
1, 45	Bis(2-chloroisopropyl) ether	0.05	50	50
1, 128	2-chlorophenol	0.05	50	50
1, 146	1,3-dichlorobenzene	0.05	50	50
1,146 ,C	1,4-dichlorobenzene	0.05	30	20
1, 146	1,2-dichlorobenzene	0.05	50	50
1, 112	2-flurorphenol (surrogate)	0.05	50	50
1, 117	Hexachloroethane	0.05	50	50
1, 107	2-methylphenol	0.05	50	50
1, 107	4-methylpenol	0.05	50	50
1,70 ,S	n-nitroso-di-n-propylamine	0.05	50	50
1,94 ,C	Phenol	0.05	30	20
1, 99	Phenol-d6	0.05	50	50
2, 93	Bis(2-chloroethoxy) methane	0.05	50	50
2, 127	4-chloroaniline	0.05	50	50
2,107 ,C	4-chloro-3-methylphenol	0.05	30	20
2,162 ,C	2,4-dichlorophenol	0.05	30	20
2, 225,C	Hexachlorobutadiene	0.05	30	20
2, 82	Isophorone	0.05	50	50
2, 142	2-methylnaphthalene	0.05	50	50
2, 128	Naphthalene	0.05	50	50
2, 77	Nitrobenzene	0.05	50	50
2, 82	Nitrobenzene-d8 (surrogate)	0.05	50	50
2,139 ,C	2-nitrophenol	0.05	30	20
2, 180	1,2,4-trichlorobenzene	0.05	50	50
3,154 ,C	Acenaphthene	0.05	30	20
3, 152	Acenaphthylene	0.05	50	50
3, 162	2-chloronaphthalene	0.05	50	50
3, 204	4-chlorophenyl phenyl ether	0.05	50	50
3, 168	Dibenzofuran	0.05	50	50
3, 149	Diethyl phthalate	0.05	50	50
3, 163	Dimethyl phthalate	0.05	50	50
3,184 ,S	2,4-dinitrophenol	0.05	50	50
3, 165	2,4-dinitrotoluene	0.05	50	50
3, 162	2,6-dinitrotoluene	0.05	50	50
3, 166	Fluorene	0.05	50	50
3, 172	2-flurorbiphenyl (surrogate)	0.05	50	50
3,237 ,S	Hexachlorocyclpentadiene	0.05	50	50

3, 65	2-nitroaniline	0.05	50	50
3, 138	3-nitroaniline	0.05	50	50
3, 138	4-nitroaniline	0.05	50	50
3,139 ,S	4-nitrophenol	0.05	50	50
3, 330	2,4,6-tribromophenol (surrogate)	0.05	50	50
3, 196,C	2,4,6-trichlorophenol	0.05	30	20
3, 196	2,4,5-trichlorophenol	0.05	50	50
4, 178	Anthracene	0.05	50	50
4, 248	4-bromophenyl phenyl ether	0.05	50	50
4, 149	di-n-butyl phthalate	0.05	50	50
4, 198	4,6-dinitro-2-methyl-phenol	0.05	50	50
4,202 ,C	Fluoranthene	0.05	30	20
4, 284	Hexachlorobenzene	0.05	50	50
4, 169,C	N-nitrosodiphenylamine	0.05	30	20
4, 266,C	Pentachlorophenol	0.05	30	20
4, 178	Phenanthrene	0.05	50	50
5, 228	Benzo(a)anthracene	0.05	50	50
5, 149	Bis(2-ethylhexyl) phthalate	0.05	50	50
5, 149	Butyl benzyl phthalate	0.05	50	50
5, 228	Chrysene	0.05	50	50
5, 252	3,3'-dichlorobenzidine	0.05	50	50
5, 202	Pyrene	0.05	50	50
5, 244	Terphenyl-d14 (surrogate)	0.05	50	50
5, 149	di-n-octyl phthalate	0.05	50	50
5, 276	Indeno(1,2,3-cd)pyrene	0.05	50	50
6, 252	Benzo(b)fluoroanthene	0.05	50	50
6, 252	Benzo(k)fluroanthene	0.05	50	50
6, 276	Benzo(g,h,I)perylene	0.05	50	50
6, 252,C	Benzo(a)pyrene	0.05	30	20
6, 278	Dibenz(a,h)anthracene	0.05	50	50
	Carbazol	0.05	50	50

Note:
Internal standards are suggested; internal standards used must have retention times that are closest to the analytes:
1 – 1,4-dichlorobenzene-d4
2 – naphthalene-d8
3 – acenaphthene-d10
4– phenanthrene-d10
5 – chrysene-d12
6- perylene-d12

8.3 List all initial calibrations and samples qualified due to calibration excursions.

INSTRUMENT ID:

Unique IC ID	Date	Compound	RRF [control limit] %RSD [control limit]	Action	Samples Affected (client/lab ID)

9.0 CONTINUING CALIBRATION

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Continuing calibration checks satisfactory performance of the instrument on a day-to-day basis. The initial calibration is verified once every 12 hours.

For 8270, a calibration standard near the midpoint concentration of the calibration range must meet the verification criteria.
The system performance check compounds (SPCCs), which are evaluated for compound stability and degradation caused by contaminated lines or active sites in the system, must meet mean response factor criteria of 0.05: n-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol.
The calibration check compounds (CCCs), which are evaluated for integrity of the system; high variability may indicate system leaks or reactive sites on the column, acenaphthene, 1,4-dichlorobenzene, hexachlorobutadiene, n-nitroso-diphenylamine, di-n-octyl phthalate, fluoranthene, benzo(a)pyrene, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2-nitrophenol, phenol, pentachlorophenol, 2,4,6-trichlorophenol, must be equal to or less than 20% D, where %D is percent difference when performing the average response factor calibration and percent drift when using a regression calibration. Corrective action must be taken if these criteria are not met prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project, and not included in the standards, all analytes must meet the 20% D criterion.

The retention time of the internal standards must not change by more than 30 seconds from that in the mid-point standard of the most recent initial calibration sequence. Otherwise, corrections must be made and the samples analyzed under this calibration must be reanalyzed. The area of the internal standards must not change by a factor of two (-50% to +100%) from that in the mid-point standard of the most recent initial calibration sequence. Otherwise corrections must be made and the samples analyzed under this calibration must be reanalyzed.

9.1 Were continuing calibration standards analyzed for every twelve hours of sample analysis, for each analyte, for each GC/MS?

VALIDATION ACTIONS:
Check QAPP criteria for remaining compounds.

a. If no, contact laboratory for explanation and review in data completeness section. Reject associated sample data (R) if continuing calibration data cannot be provided.
b. If RRF <criteria (SPCC, QAPP for remaining compounds) reject sample detection limits (R) and approximate detected results (J) for the affected compounds.
c. If %D > criteria (CCC, QAPP for remaining compounds) approximate detected and non-detected sample results (UJ, J).

9.2 Check for transcription/calculation errors; check a minimum of one compound/internal standard to verify that calibration factors and %Ds have been calculated correctly using the specified internal standard. Request corrections from the laboratory. Show calculation below.

9.3 List below all continuing calibrations and samples qualified due to continuing calibration excursions.

INSTRUMENT ID:

Unique CC ID	Date	Compound	RRF [control limit] %D [control limit]	Action	Samples Affected (client and lab ID)

10.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity; (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

For 8270, Internal standards **may** be monitored in all samples, blanks, and standards. The QAPP should be consulted to determine if internal standard evaluation is required for the project. Use internal standards 1,4-dichlorobenzene-d4, napthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 or other compounds that have similar retention times at 40 ng/µL or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.2 relative to the internal standards. Area is used to calculate response factors. Use the internal standard used for calculation should have a retention time closest to the analyte.

10.1 Were internal standard areas of samples or blanks within +100% or -50% of the internal standard associated with the continuing calibration standard?

10.2 Check that correct internal standard data from the calibration standard is used for comparison. If errors are present, a more in-depth review of the data is required. Summarize necessary corrections.

Note: The laboratory is required to reanalyze field, QC, and blank samples when internal standard criteria are not met.

VALIDATION ACTIONS:

a. If area count is above the limit, approximate (J) detected results for compounds quantitated with that internal standard.
b. If area count is below limits, approximate detected and non-detected results (UJ,J) for compounds quantitated with that internal standard.
c. If extremely low area counts are reported (<10%), flag associated detection limits as rejected (R), approximate detected results (J).

10.2 Are retention times of the internal standards within 30 seconds of the associated calibration standard?

VALIDATION ACTION:
If retention times are outside criteria, reject undetected results (R) for compounds quantitated with that internal standard. Be aware that false positive and negative results may exist so carefully examine chromatographic profile.

10.3 Were samples and method blanks reanalyzed when internal standard criteria was exceeded?

VALIDATION ACTION: Document in the narrative report that the laboratory was not in compliance with analytical method requirements.
If yes, and internal standard areas remain outside criteria, validate both sets of sample data with respect to above actions.

If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

a. Magnitude and direction of the IS area shift.
b. Magnitude and direction of the IS retention time shift.
c. Technical holding times.
d. Comparison of the values of the target compounds reported in each fraction.
e. Other QC results.

10.4 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Range (area)	Action

Note:
Internal standard 1,4-dichlorobenzne-d4 (14DCB)applies to :Bis(2-chloroethyl) ether, Bis(2-chloroisopropyl) ether, 2-chlorophenol, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 2-flurorphenol (surrogate),
Hexachloroethane, 2-methylphenol, 4-methylpenol, n-nitroso-di-n-propylamine, Phenol, Phenol-d6

Internal standard naphthalene-d8 (ND) applies to: 2-Bis(2-chloroethoxy) methane, 4-chloroaniline, 4-chloro-3-methylphenol, 2,4-dichlorophenol, Hexachlorobutadiene, Isophorone, 2-methylnaphthalene, Naphthalene,
Nitrobenzene, Nitrobenzene-d8 (surrogate), 2-nitrophenol, 1,2,4-trichlorobenzene

Internal standard acenaphthene-d10 (AN) applies to: Acenaphthene, Acenaphthylene, 2-chloronaphthalene, 4-chlorophenyl phenyl ether, Dibenzofuran, Diethyl phthalate, Dimethyl phthalate, 2,4-dinitrophenol, 2,4-dinitrotoluene, 2,6-dinitrotoluene, Fluorene, 2-flurorbiphenyl (surrogate), Hexachlorocyclpentadiene, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 2,4,6-tribromophenol (surrogate), 2,4,6-trichlorophenol, 2,4,5-trichlorophenol

Internal standard phenanthrene-d10 (PH) applies to: Anthracene, 4-bromophenyl phenyl ether, di-n-butyl phthalate, 4,6-dinitro-2-methyl-phenol, Fluoranthene, Hexachlorobenzene, N-nitrosodiphenylamine, Pentachlorophenol, Phenanthrene

Internal standard chrysene-d12 (C) applies to: Benzo(a)anthracene, Bis(2-ethylhexyl) phthalate, Butyl benzyl phthalate, Chrysene, 3,3'-dichlorobenzidine, Pyrene, Terphenyl-d14 (surrogate), di-n-octyl phthalate,
Indeno(1,2,3-cd)pyrene

Internal standard perylene-d12 (P) applies to: Benzo(b)fluoroanthene, Benzo(k)fluroanthene, Benzo(g,h,I)perylene, Benzo(a)pyrene, Dibenz(a,h)anthracene

11.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

11.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD

12.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION AND SYSTEM PERFORMANCE

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present). The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand, represent an absence of data and are, therefore, more difficult to assess. One example of detecting false negatives is not reporting a Target Compound that is reported as a TIC.
For quantitation evaluation, the objective is to ensure that the reported quantitation results and the detection limits are accurate.

For 8270, samples should be screened to minimize contamination of the instrument. Dilutions are performed to keep the analyte concentration in the upper half of the calibration range. The qualitative identification of analytes is based on retention time, and on comparison of the sample mass spectrum to a reference mass spectrum generated by the lab using the conditions of the method.
1. The relative retention times (RRTs) must be within +0.06 RRT units of the standard RRT.
2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:
a. The characteristic ions are the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum
b. The relative intensities of the characteristic ions must agree within ± 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)
c. Structural isomers that produce similar mass spectra should be identified as individual isomers if they have different retention times. Resolution is achieved if the height of the valley between two peaks is less than 25% of the sum of the two peak heights.
d. Identification is hampered when sample components are not resolved and produce mass spectra containing ions contributed by more than one analyte. Appropriate selection of sample spectra and background spectra is important.
e. Examination of extracted ion current profiles can aid in the selection of spectra. When analytes coelute the identification may be met, but each spectrum will contain extraneous ions contributed by the coeluting compound.

12.1 Were the SVOC reconstructed ion chromatograms, the mass spectra for the identified compounds, and the data system printouts included?
If no, contact laboratory and summarize problems/resolutions in data completeness section.

12.2 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other_____?
ACTIONS: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement in quality data.

12.3 Was the RRT of each reported compound within criteria?

RRT= RT analyte/RT internal standard

12.4 Did all the ions present in the mass spectrum meet criteria?
Note: If ions >10% in the sample spectrum are not present in the standard spectrum, verify that these have been accounted for by the analyst.

12.5 Were sample and standard relative intensities within criteria?
ACTIONS: If no, for any of the above, use professional judgement to determine acceptability of data. If it is determined that incorrect identifications were made, all such data should be rejected (R) or changed to non-detected (U). Summarize qualifications performed below and in the narrative report.

12.6 Were samples reanalyzed at the appropriate dilution, when saturation occurred or when concentrations exceeded linear range of the calibration curve?
Note: When sample dilution is performed, the laboratory typically reports two sets of sample data, diluted sample with responses within linear range and undiluted sample (least diluted sample is reported if two sets of dilutions were performed).
ACTION: Sample results quantitated with responses that exceed calibration range are approximated (J). In addition, depending on data quality objectives of the project, reanalysis of diluted extract may be required. Review resolutions in the narrative report.

12.7 Were correct quantitation ion, internal standard and RF used?

12.8 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions and for soils, sample moisture?
ACTIONS: If no and errors are large, request resubmittal of data package.

Sample calculation:
For 8270 Concentration (µg/L) = [Area analyte * Conc IS * Dilution factor * Vol of extract (µl)]
/[Area IS*RF from IC *Volume sample extracted (ml)] * 1000
Concentration (µg/Kg) = [Area analyte * Conc IS * Dilution factor * Vol of extract injected (µl)]
/[Area IS*RF from IC *weight sample (g)] * 1000

12.9 Were compounds detected at concentrations below CRQL (or PQL) reported and qualified as approximate (J)?
ACTIONS: If no, make necessary corrections. Summarize results of raw data review below.

12.10 Was the complete target compound list reported for each sample result?
ACTIONS: If no, request corrections from the laboratory. Summarize necessary corrections.

Document which sample analyses were reviewed and indicate frequency of raw data review. Approximately 10% of data should be verified through raw data review. Show calculations below.

13.0 TENTATIVELY IDENTIFIED COMPOUNDS (TICs)

Note: TICs may not be required for the project. If required for the project, non-target analytes of apparent greatest concentration may be tentatively identified via library search.

Chromatographic peaks in volatile analyses, including blanks, that are not target analytes, surrogates, or internal standards are potential tentatively identified compounds (TICs). TICs must be qualitatively identified via a forward search of the Spectral Library, and the identifications assessed by the data reviewer.

For each sample, the laboratory must conduct a mass spectral search of the library and report the possible identity for the appropriate number of the largest volatile fraction peaks which are not surrogates, internal standard, or target compounds, but which have area or height greater than the area or height of the nearest internal standard.

Guidelines for tentative identification are as follows:
a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.
b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.
c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target compounds.
e. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Library reductions can sometimes create these discrepancies.

The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.
Examples:
a. Common laboratory contaminants: CO (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 µg/L or 4000 µg/Kg.
b. Solvent preservatives, such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.
c. Aldol reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

Occasionally, a target compound may be identified as a TIC in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected. TIC results, which are not sufficiently above the level in the blank, should not be reported.

13.1 Was library searching required for the project?
13.2 Were Tentatively Identified Compounds properly identified with scan number or retention time, estimated concentration?
13.3 Were the mass spectra for TICs and associated "best match" spectra included?
13.4 Were each of the ions present in the reference mass spectra with a relative intensity greater than 10% also present in the sample mass spectrum?
13.5 Did TIC and "best match" standard relative ion intensities agree within 20%?

Use professional judgement to determine acceptability of TIC identifications. If it is determined that an incorrect identification was made, note in below qualifications made to the sample data.

13.6 Were TICs quantitated using the closest internal standard free of contamination?
Actions: If no, note corrections below, if errors are large, request resubmittal of data package:

ACTIONS:
1. All TIC results should be qualified "NJ", tentatively identified, with approximated concentrations.
2. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.
3. If all peaks were not library searched and quantitated, these data are requested from the laboratory.
4. If errors are large, request resubmittal of data package.

13.7 Summarize TICs qualified as a result of TIC excursions, if required.

Sample ID	TIC	Concentration

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form - USEPA Method 8270C Semivolatile Organics
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ PARTIAL VALIDATION
Method reference: USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington. D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8270C	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3510C 3550B 8270	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
For Analyses of Semivolatile Organics by USEPA SW-846 Method 8270C

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8270C. (National Functional Guidelines and Region V guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is Not Reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR SEMIVOLATILE ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues regarding problems with sample receipt or condition of samples.

1.2 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as approximate (J). If a soil sample other than TCLP contains more than 90% water, all data should be rejected (R).

1.3 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.4 List below any communication with laboratory regarding problems with data completeness, reference to data, contact person, specific problems and resolutions (This would include QC forms etc).

1.5 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8270: Aqueous samples must be extracted within 7 days of collection and soil/sediment samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples must be stored at 4°C ±2.

VALIDATION ACTIONS:

a. If extraction holding times are exceeded, associated sample results are flagged as approximate (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as approximate (J) and non-detected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates, prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries. The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

Surrogates are added such that 1 milliliter aliquot added to 1 liter of sample is equal to the concentration of 10 times the quantitation limit or near the mid-point of the calibration curve. If GPC is used, 2 milliliters are added to samples.
If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries cannot be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Any time there are two or more analyses for a particular fraction the reviewer must determine which are the best data to report. Considerations should include but are not limited to:
a. Surrogate recovery (marginal versus gross deviation).
b. Technical holding times.
c. Comparison of the values of the target compounds reported in each fraction.
d. Other QC information, such as performance of internal standards.

Semi-volatile surrogates are grouped as follows:

- Acid extractable: phenol-d6, 2-fluorophenol, and 2,4,6-tribromophenol.
- Base neutral: nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14.

VALIDATION ACTIONS: Qualification of data is necessary if two or more base-neutral or acid surrogates are out of control limits or if any one surrogate compound has a recovery <10%.

a. If %recovery is <10%, flag positive results as approximate (J) and reject detection limits, (R).
b. If %recovery is 10% to lower control limit, flag associated sample results and detection limits as approximate (UJ, J).
c. If %recovery is > upper control limit, flag **positive** results as approximate (J).
d. If one acid or base surrogate has a recovery >10%, but less than the lower limit and another acid or base has a recovery greater than the upper limit, flag positive results and detection limits as approximate (J, UJ).
e. If surrogates are not used, contact laboratory for explanation and describe problems/resolutions in final narrative report. Alert the Project Manager immediately.
f. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with method requirements.
g. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
h. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.2 List below samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:
PD6 - phenol-d6
2FP - 2-fluorophenol
246TP - 2,4,6-tribromophenol.
NB – nitrobenzene-d5
2FBP - 2-fluorobiphenyl
TP - terphenyl-d14

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate the effects of sample matrix on method performance. Representative compounds are spiked into a field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?

4.2 Was laboratory batch QC performed?

For 8270 - At a minimum, the target compounds 1,2,4-trichlorobenzene, acenaphthene, 2,4-dinitrotoluene, pyrene, n-nitroso-di-n-propylamine, 1,4-dichlorobenzene, pentachlorophenol, phenol, 2-chlorophenol, 4-chloro-3-methylphenol, and 4-nitrophenol must be included in the spiking solutions. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. The concentration of the spike solution should be base/neutrals at 100 mg/L and acids at 200 mg/L for water and soil samples, and five times higher for waste samples. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are approximated (J).

b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.

c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).

d. If RPD criteria are not met, approximate **detected** results (J) and approximate non-detected results (UJ).

e. If complete fractions (acid/base) have recovery problems, all the target analytes in that fraction may be qualified if the MS did not contain all target analytes.

f. If MS/MSDs were not analyzed, contact the laboratory for an explanation and describe the problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

g. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.2 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed for 8270 analysis to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contamination.

Note: B flags applied by the lab should not be removed from Form 1s.
6.1 Were method blanks analyzed for each group of samples of similar matrix?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination cannot be made. Alert the Project Manager immediately. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: Equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

6.4 If inordinate numbers of target compounds are found at low levels in the blank(s), it may be indicative of a problem and should be noted for action.

Action levels are calculated at 5x blank (method) value (10x for phthalates). Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.
Instrument blanks should be analyzed after high concentrations, otherwise carryover may be suspected. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

VALIDATION ACTIONS:
Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the data validation report.
If the sample concentration (extract) is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".

b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration with a "U".

c. If the sample concentration is > Action level, qualification of data is not necessary.

6.5 Summarize all blanks and any samples qualified due to blank contamination.
Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity; (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

For 8270, Internal standards **may** be monitored in all samples, blanks, and standards. The QAPP should be consulted to determine if internal standard evaluation is required for the project. Use internal standards 1,4-dichlorobenzene-d4, napthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 or other compounds that have similar retention times at 40 ng/µL or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.2 relative to the internal standards. Area is used to calculate response factors. Use the internal standard used for calculation should have a retention time closest to the analyte.

7.1 Were internal standard areas of samples or blanks within +100% or -50% of the internal standard associated with the continuing calibration standard?

Note: The laboratory is required to reanalyze field, QC, and blank samples when internal standard criteria are not met.

VALIDATION ACTIONS:

a. If area count is above the limit, approximate (J) detected results for compounds quantitated with that internal standard.
b. If area count is below limits, approximate detected and nondetected results (UJ,J) for compounds quantitated with that internal standard.
c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R), approximate detected results (J).

7.2 Are retention times of the internal standards within 30 seconds of the associated calibration standard?

VALIDATION ACTION:
If retention times are outside criteria, reject undetected results, R, for compounds quantitated with that internal standard. Be aware that false positive and negative results may exist so carefully examine chromatographic profile.

7.3 Were samples and method blanks reanalyzed when internal standard criteria was exceeded?

VALIDATION ACTION: Document in the narrative report that the laboratory was not in compliance with analytical method requirements.
If yes, and internal standard areas remain outside criteria, validate both sets of sample data with respect to above actions.

If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:
a. Magnitude and direction of the IS area shift.
b. Magnitude and direction of the IS retention time shift.
c. Technical holding times.
d. Comparison of the values of the target compounds reported in each fraction.
e. Other QC results.

7.4 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Range (area)	Action

Note:
Internal standard 1,4-dichlorobenzne-d4 (14DCB)applies to :Bis(2-chloroethyl) ether, Bis(2-chloroisopropyl) ether, 2-chlorophenol, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 2-flurorphenol (surrogate),
Hexachloroethane, 2-methylphenol, 4-methylpenol, n-nitroso-di-n-propylamine, Phenol, Phenol-d6

Internal standard naphthalene-d8 (ND) applies to: 2-Bis(2-chloroethoxy) methane, 4-chloroaniline, 4-chloro-3-methylphenol, 2,4-dichlorophenol, Hexachlorobutadiene, Isophorone, 2-methylnaphthalene, Naphthalene,
Nitrobenzene, Nitrobenzene-d8 (surrogate), 2-nitrophenol, 1,2,4-trichlorobenzene

Internal standard acenaphthene-d10 (AN) applies to: Acenaphthene, Acenaphthylene, 2-chloronaphthalene, 4-chlorophenyl phenyl ether, Dibenzofuran, Diethyl phthalate, Dimethyl phthalate, 2,4-dinitrophenol, 2,4-dinitrotoluene, 2,6-dinitrotoluene, Fluorene, 2-flurorbiphenyl (surrogate), Hexachlorocyclpentadiene, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 2,4,6-tribromophenol (surrogate), 2,4,6-trichlorophenol, 2,4,5-trichlorophenol

Internal standard phenanthrene-d10 (PH) applies to: Anthracene, 4-bromophenyl phenyl ether, di-n-butyl phthalate, 4,6-dinitro-2-methyl-phenol, Fluoranthene, Hexachlorobenzene, N-nitrosodiphenylamine, Pentachlorophenol, Phenanthrene

Internal standard chrysene-d12 (C) applies to: Benzo(a)anthracene, Bis(2-ethylhexyl) phthalate, Butyl benzyl phthalate, Chrysene, 3,3'-dichlorobenzidine, Pyrene, Terphenyl-d14 (surrogate), di-n-octyl phthalate,
Indeno(1,2,3-cd)pyrene

Internal standard perylene-d12 (P) applies to: Benzo(b)fluoroanthene, Benzo(k)fluroanthene, Benzo(g,h,l)perylene, Benzo(a)pyrene, Dibenz(a,h)anthracene

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD

Section 3

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8081A Organochlorine Pesticides – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8081A Organochlorine Pesticides – Partial Validation

O'Brien & Gere Engineers Data Validation Form
USEPA Method 8081A Organochlorine Pesticides
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ FULL VALIDATION
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8081A	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8081A	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses for Pesticides by USEPA SW-846 Method 8081A

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8081A. (National Functional Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR PESTICIDE ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of pesticide data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, ug/L for waters and ug/kg for soils?

1.4 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.5 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.6 Was appropriate clean up used - florisil (method 3620), alumina (method 3610), silica gel (method 3630), gel permeation chromatography (GPC) (method 3640), sulfur (method 3660)?
Note: The appropriate clean up depends on the nature of the matrix interference and the target analytes.
Phthalate esters are removed by alumina, GPC or silica gel cleanup.
Aliphatic compounds, aromatic, and nitrogen-containing compounds are removed by florisil.
Sulfur is removed by sulfur cleanup.
Waxes, lipids, other high molecular weight materials are removed by GPC cleanup.
Organophosphorus pesticides are removed by GPC.
Chlorophenols, non-polar analytes (organochlorine pesticides, PAHs, nitrosamines) are removed by silica gel, florisil, or alumina cleanup.
PCBs are removed by utilizing methods 3620 and 3630 for sample preparation.

1.7 Was single-column and second analysis by GC or GC/MS used or dual-column analysis used?

1.8 Were any of the samples diluted? Were dilutions performed when necessary? Note if samples were combined due to dilutions.

1.9 Were raw data to support analyses and QC operations present and complete?

Actions: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.10 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.11 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8081A: Aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

Validation Actions:

a. If extraction holding times are exceeded associated sample results are flagged as estimated (UJ,J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than 2 times the criteria, nondetected sample results are rejected, (R), and detected sample results are approximated (J).

2.2 Summarize below the samples qualified for holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of target and/or non-target analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment Laboratory generated control limits are used to evaluate the recoveries. For 8081A, 2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl are used.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?
3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

Surrogates are added such that 1 milliliter aliquot added to 1 liter of sample is equal to the concentration of 10 times the quantitation limit or near the mid-point of the calibration curve. If GPC is used, 2 milliters is added to samples. If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Percent recovery = conc found/conc spiked * 100

3.3 Were the retention times of both of the surrogates in standards, blanks and samples within the calculated retention time windows?
3.4 Was interference present in the surrogate peak?

Validation Actions: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, and no interference is present, flag positive results as estimated (J) and reject detection limits (R).
b. If %recovery is 10% to lower control limit, and no interference is present, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, and no interference is present, flag positive results as estimated (J).
d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.
e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with method requirements.
f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of

sample data. Validate both sets of samples results and qualify data

g. If surrogate retention times in standards, samples, and blanks are outside of the retention time window, flag associated sample results and detection limits as estimated (UJ,J).

h. If interference was present, qualification of samples due to surrogate excursions is not performed.

i. If zero pesticide surrogate recovery is reported, the reviewer should examine the sample chromatogram to determine if the surrogate may be present, but slightly outside its retention time window. If this is the case, in addition to assessing surrogate recovery for quantitative bias, the overriding consideration is to investigate the qualitative validity of the analysis. If the surrogate is not present, qualify all nondetected target compounds as unusable (R).

j. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.5 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:

TCMX- 2,4,5,6-tetrachloro-m-xylene

DCBP – decachlorobiphenyl

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections

For 8081 - The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

Validation Actions: Qualification is limited to the unspiked sample only.
RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and nondetected results are approximate (UJ)..
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.4 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed for 8081 analysis to ensure that the GC system and solvents used are free of contamination.

Note for Region V, no "B" flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used to qualify samples; the detected contaminants are documented in the data validation report.
6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

There may be instances when little or no contamination was present in the associated blanks, but qualification of the sample was deemed necessary. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. However, if the reviewer determines that the contamination is from a source other than the sample, the data should be qualified. In this case, the "5x" rule does not apply; the sample value should be reported as a non-detected target compound, "U". An explanation of the rationale for this determination should be provided in the validation report.

If gross contamination exists (e.g., saturated peaks, "hump-o-grams", "junk" peaks), all affected compounds in the associated samples should be qualified as unusable (R), due to interference. This should be noted in the data validation, and as an action item if the contamination is suspected of having an effect on the sample results.

If inordinate amounts of target pesticides, Toxaphene, or other interfering non-target compounds are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted for action.

If an instrument blank was not analyzed following a sample analysis, which contained an analyte(s) at high concentration(s), sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification(s), and if so, detected compound results should be qualified.

Actions levels are calculated at 5x blank (method) value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with based upon

a comparison with the associated blank having the highest concentration of a contaminant. Instrument blanks should be analyzed after high concentrations; otherwise carryover may be suspected.

Validation Actions:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.3 List all blanks and samples qualified due to blank contamination.
Note for Region V: Equipment/Field blanks are not used for qualification of samples; list the contaminants only.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 GC INSTRUMENT PERFORMANCE

Performance checks on the gas chromatograph with electron capture detector (GC/ECD) system are performed to ensure adequate resolution and instrument sensitivity. These criteria are not sample specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances. DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port is contaminated with residue or from metal fittings. The percent breakdown is the amount of decomposition that 4,4'-DDT and Endrin undergo when analyzed on the GC column. For Endrin, the percent breakdown is determined by the presence of Endrin aldehyde and/or Endrin ketone in the GC chromatogram. For 4,4'-DDT, the percent breakdown is determined from the presence of 4,4'-DDD and/or 4,4'-DDE in the calibration standard. Breakdown is measured at the beginning of each 12-hour
shift.

Percent Breakdown of DDT = sum of DDD, DDE/sum of DDT, DDE, and DDD * 100
Percent Breakdown of Endrin = sum of aldehyde and ketone/sum of Endrin, aldehyde and ketone * 100

Validation Action:

7.1- If 4,4'-DDT breakdown is greater than 20.0 percent:
a -Qualify all positive results for DDT with "J". If DDT was not detected, but DDD and DDE are detected, then qualify the quantitation limit for DDT as unusable (R).
b - Qualify positive results for DDD and/or DDE as presumptively present at an approximated quantity (NJ).

7.2 - If Endrin breakdown is greater than 20.0 percent:
a - Qualify all positive results for Endrin with "J". If Endrin was not detected, but Endrin aldehyde and Endrin ketone are detected, then qualify the quantitation limit for Endrin as unusable (R).
b - Qualify positive results for Endrin Aldehyde and Endrin ketone as presumptively present at an approximated quantity (NJ).

7.3 - If the combined 4,4'-DDT and Endrin breakdown is greater than 30.0 percent:
a - The reviewer should consider the degree of individual breakdown of DDT and Endrin and apply qualifiers as described above.

7.4 List below samples qualified due to breakdown excursions.

INSTRUMENT ID:

Column ID	Calibration ID - Date/Time	Analyte	Excursion	Samples affected (client/lab ID) and action

8.0 GC INITIAL CALIBRATION AND CALIBRATION VERIFICATION

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide compounds. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence and of producing a linear calibration curve.

Calibration verification checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To confirm the calibration and evaluate instrument performance, calibration verification is performed.

Calibration standards should be prepared at a minimum of five concentrations which correspond to the expected range of concentrations in the samples and should bracket the linear range of the detector. Two calibration mixtures should be prepared for the single component analytes to minimize resolution and quantitation problems on confirmation columns and to allow determination of endrin and DDT breakdown. The mixtures should be selected to minimize the problem of peak overlap. Separate single-point calibration standards near the mid-point of the calibration range are required for each multi-component target analyte (Toxaphene and Chlordane) to familiarize the analyst with the patterns and retention times on each column.
Calibration verification is performed every 12-hour shift for all target analytes. A 2 µl injection volume is recommended for each calibration standard.
Because of the sensitivity of the ECD, the injection port and column should always be cleaned prior to calibration. the GC column should be primed prior to beginning the calibration sequence due to column absorption problems. An acceptable blank should be analyzed prior to calibration.
Retention time windows are established for compound identification. Three injections of analyte single and multi-component standards over a 72 hour period. The width of the retention time window is ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. The absolute retention time for each analyte and surrogate from the calibration verification standard or the mid-point initial calibration standard establishes the center of the retention time window. Each analyte in each standard must fall within its retention time window.
Internal standard (pentachloronitrobenzene or 1-bromo-2-nitrobenzene) may be used as internal standards at 50 µg/L concentration. In most cases, external standard calibration is used due to the sensibility of the ECD and the probability of the internal standard being affected by interferences. If internal standards are used, the area of the internal standard must be no more than 50 %D from the average area established during calibration.
Either single-column or dual column analysis may be performed. Compound identification based on single-column should be confirmed on a second column or GC/MS Method 8270 can be used. The dual-column option allows one injection to be used; this technique may not be appropriate when the instrument is subject to mechanical stress, many samples are to be analyzed in a short time period, or when contaminated samples are analyzed.
Two µl injections are used for sample extracts.

The Percent Relative Standard Deviation (%RSD) of the calibration factors for each of the single component pesticides and surrogates in the initial calibration on both columns must be less than or equal to 20.0 percent. Otherwise, a calibration curve or a non-linear calibration (polynomial equation) must be used.

Linear calibration using least squares regression – If the RSD is greater than 20%, or if the analyst so chooses, linearity through the origin cannot be assumed and a linear regression of response verses concentration equation that does not pass through the origin may be used. The instrument response is dependent variable (y) and the concentration is the independent variable (x). The regression will produce the slope and intercept for a linear equation (y=mx+b) where y is the peak area, m is the slope, x is the concentration and b is the intercept. The origin is not forced through zero and do not use the origin as the sixth calibration point. The regression calculation will result in the correlation coefficient – r –, which is a measure of the "goodness of fit". A value of 1.00 is perfect, and for quantitative purposes, r must be greater than or equal to 0.99.

Non-linear calibration – if other approaches don't meet criteria, no more than third order non-linear may be used. First order (linear) requires five standards, second order (quadratic) model requires six standards and third order requires seven standards. The "goodness of fit" of the polynomial equation is evaluated by the weighted coefficient of the determination (COD), which must be greater than 0.99.

Calibration verification is performed every 12-hour shift for all target analytes. Analysts should alternate the use of high and low

concentration mixtures of single and multi-component analytes. A calibration standard must be injected at not less than every 20 samples (every 10 is recommended) and at the end of the analytical sequence. Injections of method blanks, MS, and other non-standards are counted towards the 20 "samples". The calibration factor should not exceed ± 15% difference or drift, where %D is percent difference when performing the average response factor calibration and percent drift when using a regression calibration. If the %D of target analytes is greater than 15%, the calibration may be acceptable if the mean of the %Ds for all analytes is less than or equal to 15%. This approach will lead to greater uncertainty for those analytes for which the %D is greater than 15%. Otherwise, a new calibration must be performed. When calibration verification standard fails criteria, all samples injected after the last standard that met criteria may be re-injected. If the standard analyzed after samples exhibits a high response with a %D greater than 15%, and the analyte was not detected, reanalysis is not required. If the analyte was detected, re-analysis is required. If the standard analyzed after samples exhibits a low response with a %D greater than 15%, and the analyte was not detected, reanalysis is required to determine if false negative results were reported.

Tentative identification of analytes occurs when a peak in the sample extract falls within the retention time window. Each identification must be confirmed using either a second dissimilar GC column or another technique (GC/MS). The agreement between concentrations should be less than 40% RPD. The higher of the two concentrations should be reported. If one result is significantly higher, check for overlapping peaks and baseline. If no problems are found, report the higher result and note in the case narrative.

GC/MS confirmation will require 10 ng/µg in the final extract.

Identification of Chlordane is based on characteristic fingerprint retention times and peak shapes and quantitation is based on the area under the peaks as compared to the area under the corresponding calibration peaks of the same retention time and shapes in the standards. Quantitate using either total area of the pattern, using 3 to 5 major peaks, or report alpha or gamma chlordane and heptachlor separately.

Identification of Toxaphene is based on characteristic fingerprint retention times and peak shapes and quantitation is based on the area under the peaks as compared to the area under the corresponding calibration peaks of the same retention time and shapes in the standards. Adjust the sample size so that the major peaks are 10-70% of the full scale. Inject a standard that is within 10 ng of the sample amount. Quantitate using total area of the pattern or using 4 to 6 major peaks.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass in nanograms

Concentration (µg/L) = Area analyte * Conc IS * Dilution factor * Vol of extract (µl)
/Area IS*mean CF (IC) *Vol sample extracted (ml) * 1000
Concentration (µg/Kg) = Area analyte * Conc IS * Dilution factor * Vol of extract injected (µl)
/Area IS*mean CF (IC) *weight sample (g) * 1000

Check for transcription/calculation errors for calibration factors, %RSDs, and %Ds. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

8.1 Validation Action:

a - If retention time windows, are not calculated correctly, contact laboratory for corrected resubmission of the data package with corrected windows; use the corrected values for all evaluations.
b - If the sample concentration exceeds the linearity of the calibration curve, and the sample is not properly diluted and re-analyzed, flag the positive results "J".
c -If the standard concentration criteria are not met, flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".
d - If the %RSD criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".
e - If the %D criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".
f - Do all standard retention times fall within the windows established during the Initial Calibration?
ACTION: If no, associated samples in the entire analytical sequence are potentially affected. Check to see if the

sample chromatograms contain peaks within an expanded window surrounding the expected retention times. If no peaks are found and the surrogates are visible, non-detects are valid. If peaks are present and cannot be identified through pattern recognition or using a revised RT window, qualify all positive results "JN" and non-detects as unusable (R). If the retention time windows are grossly exceeded, this should be noted in the data validation report. Retention time windows should be checked for calculation errors and corrections should be requested from the laboratory.

g – Was the correct analytical sequence used for calibration analyses for single component pesticides and multi component analytes?

h - If two columns were used to report sample results, only qualify if calibration excursions are detected on both columns.

ACTION: If no flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

8.2 List below all initial calibrations and samples qualified due to initial calibration excursions.

INSTRUMENT ID:

Column ID	Calibration ID - Date/Time	Analyte	Excursion Retention time %RSD	Samples affected (client/lab ID) and action

9.0 CLEANUP VERIFICATION

Pesticide cleanup procedures are utilized to remove matrix interferences from sample extracts prior to analysis. The use of the Florisil cartridge cleanup procedure significantly reduces matrix interferences caused by polar compounds. Gel permeation chromatography (GPC) is used to remove high molecular weight contaminants that can interfere with the analysis of target analytes. Pesticide cleanup procedures may be checked by spiking the cleanup columns and cartridges, and verifying the recovery of pesticides through the cleanup procedure.

Lot numbers of Florisil cartridges used for sample cleanup may be checked by spiking with 2,4,5-trichlorophenol and the midpoint concentration of a standard. The lot of Florisil cartridges is acceptable if the recoveries for all of the pesticides and surrogates are within 80 to 120 percent, if the recovery of 2,4,5-trichlorophenol is less than 5 percent, and if no peaks interfering with the target analytes are detected.

GPC is used for the cleanup of all soil sample extracts and for water sample extracts that contain high molecular weight components that interfere with the analysis of the target analytes. At least once every 7 days, the calibration of the GPC unit may be checked by spiking with the matrix spiking solution. The GPC calibration is acceptable if the recovery of the pesticides in the matrix spiking solution are within 80 to 110 percent. A GPC blank is analyzed after each GPC calibration and is acceptable if the blank does not exceed one-half the CRQL for any target analytes.

VALIDATION ACTION:

a - If Florisil Cartridge Check criteria are not met, the raw data should be examined for the presence of polar interferences and flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

b - If Gel Permeation Criteria are not met, the raw data should be examined for the presence of high molecular weight contaminants, subsequent sample data should be examined for unusual peaks, and flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

c - If zero recovery was obtained for the pesticide compounds and surrogates during either check, then the non-detected target compounds may be suspect and the data may be qualified unusable (R).

d - If high recoveries (i.e., greater than 120%) were obtained for the pesticides and surrogates during either check, flag associated positive quantitative results with "J". Non-detected target compounds do not require qualification.

9.1 List below samples qualified due to cleanup excursions.

INSTRUMENT ID:

Cleanup ID	Analyte	Excursion	Samples affected (client/lab ID) and action

10.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

10.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

11.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION AND REPORTED DETECTION LIMITS

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present). The objective is to ensure that the reported quantitative results and contract required quantitation limits (CRQLs) are accurate.

Retention time windows are established for compound identification. Three injections of analyte single and multi-component standards over a 72 hour period. The width of the retention time window is ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. The absolute retention time for each analyte and surrogate from the calibration verification standard or the mid-point initial calibration standard establishes the center of the retention time window. Each analyte in each standard must fall within its retention time window.

Either single-column or dual column analysis may be performed. Compound identification based on single-column should be confirmed on a second column or GC/MS Method 8270 can be used. The dual-column option allows one injection to be used; this technique may not be appropriate when the instrument is subject to mechanical stress, many samples are to be analyzed in a short time period, or when contaminated samples are analyzed.

Tentative identification of analytes occurs when a peak in the sample extract falls within the retention time window. Each identification must be confirmed using either a second dissimilar GC column or another technique (GC/MS). The agreement between concentrations should be less than 40% RPD. The higher of the two concentrations should be reported. If one result is significantly higher, check for overlapping peaks and baseline. If no problems are found, report the higher result and note in the case narrative. The retention times of both of the surrogates, matrix spikes, and reported compounds in each sample must be within the calculated retention time windows on both columns.

GC/MS confirmation will require 10 ng/µg in the final extract.

Identification of Chlordane is based on characteristic fingerprint retention times and peak shapes and quantitation is based on the area under the peaks as compared to the area under the corresponding calibration peaks of the same retention time and shapes in the standards. Quantitate using either total area of the pattern, using 3 to 5 major peaks, or report alpha or gamma chlordane and heptachlor separately.

Identification of Toxaphene is based on characteristic fingerprint retention times and peak shapes and quantitation is based on the area under the peaks as compared to the area under the corresponding calibration peaks of the same retention time and shapes in the standards. Adjust the sample size so that the major peaks are 10-70% of the full scale. Inject a standard that is within 10 ng of the sample amount. Quantitate using total area of the pattern or using 4 to 6 major peaks.

When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract should use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses. Chromatograms should display single component pesticides detected in the sample and the largest peak of any multicomponent analyte detected in the sample at less than full scale.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass in nanograms

Concentration (µg/L) = Area analyte * Conc IS * Dilution factor * Vol of extract (µl)
/Area IS*mean CF (IC) *Vol sample extracted (ml) * 1000

Concentration (µg/Kg) = Area analyte * Conc IS * Dilution factor * Vol of extract injected (µl)
/Area IS*mean CF (IC) *weight sample (g) * 1000

Validation Action:

Confirm reported detected analytes by comparing the sample chromatograms to the tabulated results and verifying peak measurements and retention times. Confirm reported non-detected analytes by a review of the sample chromatograms. Check the associated blank data for potential interferences (to evaluate sample data for false positives) and check the calibration data for adequate retention time windows (to evaluate sample data for false positives and false negatives).

For multi-component target compounds, the retention times and relative peak height ratios of major component peaks

should be compared against the appropriate standard chromatograms.

11.1 If the retention time criteria for both columns were not met, or if interference is present, all target compounds that are reported detected should be considered non-detected.
a. If the misidentified peak was sufficiently outside the target pesticide retention time window, then the reported values may be a false positive and should be replaced with the sample CRQL value.
b. If the misidentified peak poses an interference with potential detection of a target peak, then the reported value should be considered and qualified as unusable (R).

11.2 If the data reviewer identifies a peak in both GC column analyses that falls within the appropriate retention time windows, but was reported as a non-detect, then the compound may be a false negative. Professional judgement should be used to decide if the compound should be included. All conclusions made regarding target compound identification should be included in the data validation report.

11.3 If multi-component target compounds exhibit marginal pattern-matching quality, professional judgement should be used to establish whether the differences are due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of a multi-component pesticide is strongly suggested, results should be reported as presumptively present (N).

11.4 If GC/MS confirmation was required but not performed, the reviewer should report this in the data validation report.

11.5 Quantitation limits affected by large, off-scale peaks should be qualified as unusable (R). If the interference is on-scale, the reviewer can provide an approximated quantitation limit (UJ) for each affected compound.

11.6 Single-peak pesticide results are checked for agreement between quantitative results obtained on the two GC columns. The agreement between concentrations should be less than 40% RPD. The higher of the two concentrations should be reported. If one result is significantly higher, check for overlapping peaks and baseline. If no problems are found, report the higher result and note in the case narrative. If an interfering compound is indicated, professional judgement must be used to determine how best to report, and if necessary, qualify the data.

11.7 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other_____?
Actions: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement in quality data.

11.8 Were samples reanalyzed at the appropriate dilution, when saturation occurred or when concentrations exceed linear range of the calibration curve?
Note: When sample dilution is performed, the laboratory typically reports two sets of sample data, diluted sample with responses within linear range and undiluted sample (least diluted sample is reported if two sets of dilutions were performed).
ACTION: Sample results quantitated with responses that exceed calibration range are approximated (J). In addition depending on data quality objectives of the project reanalysis of diluted extract may be required. Review resolutions in the narrative report.

11.9 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions and for soils, sample moisture?
Actions: If no and errors are large, request resubmittal of data package.

11.10 Were compounds detected at concentrations below CRQL (or PQL) reported and qualified with a "J"? ACTIONS: If no, note in the data validation report.

Document which sample analyses were reviewed and indicate frequency of raw data review, approximately 10% of data should be verified through raw data review. Show calculation below:

ADDITIONAL NOTES

O'Brien & Gere Engineers Data Validation Form
USEPA Method 8081A Organochlorine Pesticides
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ PARTIAL VALIDATION
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8081A	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8081A	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses for Pesticides by USEPA SW-846 Method 8081A

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8081A. (National Functional Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is not reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR PESTICIDE ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues regarding problems with sample receipt or condition.

1.2 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.3 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.4 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.5 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8081A: Aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Validation Actions:

a. If extraction holding times are exceeded associated sample results are flagged as estimated (UJ,J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than 2 times the criteria, nondetected sample results are rejected, (R), and detected sample results are approximated (J).

2.2 Summarize below the samples qualified for holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of target and/or non-target analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment Laboratory generated control limits are used to evaluate the recoveries. For 8081A, 2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl are used.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

Surrogates are added such that 1 milliliter aliquot added to 1 liter of sample is equal to the concentration of 10 times the quantitation limit or near the mid-point of the calibration curve. If GPC is used, 2 milliters is added to samples. If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Validation Actions: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, and no interference is present, flag positive results as estimated (J) and reject detection limits (R).
b. If %recovery is 10% to lower control limit, and no interference is present, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, and no interference is present, flag positive results as estimated (J).
d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.
e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with method requirements.
f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
g. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.2 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:

TCMX- 2,4,5,6-tetrachloro-m-xylene

DCBP – decachlorobiphenyl

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?

For 8081 - The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

Validation Actions: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and non detected results are approximate (UJ)..
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.3 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.2 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed for 8081 analysis to ensure that the GC system and solvents used are free of contamination.

Note for Region V, no "B" flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used to qualify samples; the detected contaminants are documented in the data validation report.
6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

Actions levels are calculated at 5x blank (method) value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with based upon a comparison with the associated blank having the highest concentration of a contaminant. Instrument blanks should be analyzed after high concentrations; otherwise carryover may be suspected.

Validation Actions:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.4 List all blanks and samples qualified due to blank contamination.
Note for Region V: Equipment/Field blanks are not used for qualification of samples; list the contaminants only.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

7.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

Section 4

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8151A Chlorinated Herbicides – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8151A Chlorinated Herbicides – Partial Validation

O'Brien & Gere Engineers Data Validation Form
USEPA Method 8151A Chlorinated Herbicides
Date_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ FULL VALIDATION
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8151A	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8151A	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses for Pesticides by USEPA SW-846 Method 8151A

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data.* Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review.* EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846),* 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8151A. (National Functional Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

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Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR HERBICIDES ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of herbicide data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, ug/L for waters and ug/kg for soils?

1.4 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.5 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.6 Was appropriate clean-up of non-hydrolyzed herbicides performed?

1.7 Was a second analysis by GC or GC/MS used for confirmation used?

1.8 Were any of the samples diluted? Were dilutions performed when necessary? Note if samples were combined due to dilutions.

1.9 Were raw data to support analyses and QC operations present and complete?

Actions: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.10 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.11 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8151A: Aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

Validation Actions:

a. If extraction holding times are exceeded, associated sample results are flagged as estimated (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of target and/or non-target analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment. Laboratory generated control limits are used to evaluate the recoveries. For 8151A, 2,4-dichlorophenylacetic acid (DCAA) at a concentration of 0.5 mg/L is used.

3.1 Was the surrogate evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?
3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Percent recovery = conc found/conc spiked * 100

3.3 Were the retention times of both of the surrogates in standards, blanks and samples within the calculated retention time windows?
3.4 Was interference present in the surrogate peak?

Validation Actions: Qualification of data is necessary if the surrogate is out of control limits. If interferences are present, qualification of sample results due to surrogate excursions is not performed.

a. If %recovery is <10%, and no interference is present, flag positive results as estimated (J) and reject detection limits (R).
b. If %recovery is 10% to lower control limit, and no interference is present, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, and no interference is present, flag positive results as estimated (J).
d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.
e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with method requirements.
f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data

g. If surrogate retention times in standards, samples, and blanks are outside of the retention time window, flag associated sample results and detection limits as estimated (UJ,J).

h. If interference was present, qualification of samples due to surrogate excursions is not performed.

i. If zero pesticide surrogate recovery is reported, the reviewer should examine the sample chromatogram to determine if the surrogate may be present, but slightly outside its retention time window. If this is the case, in addition to assessing surrogate recovery for quantitative bias, the overriding consideration is to investigate the qualitative validity of the analysis. If the surrogate is not present, qualify all nondetected target compounds as unusable (R).

j. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.5 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:

DCAA – 2,4-dichlorophenylacetic acid

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

Validation Actions: Qualification is limited to the unspiked sample only.
RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). However, if the percent recovery of the compound is above the upper limit but less than 100%, the unspiked sample is not qualified.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and nondetected results are approximated (UJ).
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.4 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.2 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed for 8151A analysis to ensure that the GC system and solvents used are free of contamination. The method blank should be carried through all stages of sample preparation and measurement.

Note for Region V, no "B" flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V, equipment blanks are not used to qualify samples; the detected contaminants are documented in the data validation report.
6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.
There may be instances when little or no contamination was present in the associated blanks, but qualification of the sample was deemed necessary. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. However, if the reviewer determines that the contamination is from a source other than the sample, the data should be qualified. In this case, the "5x" rule does not apply; the sample value should be reported as a non-detected target compound, "U". An explanation of the rationale for this determination should be provided in the validation report.

If gross contamination exists (e.g., saturated peaks, "hump-o-grams", "junk" peaks), all affected compounds in the associated samples should be qualified as unusable (R), due to interference. This should be noted in the data validation, and as an action item if the contamination is suspected of having an effect on the sample results.

If inordinate amounts of target herbicides, or other interfering non-target compounds are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted for action.

If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification(s), and if so, detected compound results should be qualified.

Actions levels are calculated at 5x blank (method) value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with based

upon a comparison with the associated blank having the highest concentration of a contaminant. Instrument blanks should be analyzed after high concentrations; otherwise carryover may be suspected.

Validation Actions:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.3 List all blanks and samples qualified due to blank contamination.
Note for Region V, equipment blanks are not used to qualify samples; the detected contaminants are documented in the data validation report.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 GC INITIAL CALIBRATION AND CALIBRATION VERIFICATION

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide compounds. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence and of producing a linear calibration curve.

Calibration verification checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To confirm the calibration and evaluate instrument performance, calibration verification is performed.

Calibration standards should be prepared at a minimum of five concentrations which correspond to the expected range of concentrations in the samples and should bracket the linear range of the detector. One standard should be at a concentration near, but above, the method detection limit. Each calibration standard prepared from free acids must be derivatized. If calibration is performed using standards made from methyl ester compounds the calculation must include a correction for the molecular weight of the methyl ester versus the acid herbicide.
Retention time windows are established for compound identification. Three injections of analyte single and multi-component standards over a 72 hour period. The width of the retention time window is ± 3 times the standard deviation of the mean absolute retention time established during the 72 hour period. The absolute retention time for each analyte and surrogate from the calibration verification standard or the mid-point initial calibration standard establishes the center of the retention time window. Each analyte in each standard must fall within its retention time window. Internal standard 4,4'-dibromooctafluorobiphenyl may be used. If internal standards are used, the area of the internal standard must be no more than 50 %D from the average area established during calibration.
Either second column or GC/MS confirmation is performed.

The Percent Relative Standard Deviation (%RSD) of the calibration factors for each of the single component pesticides and surrogates in the initial calibration on both columns must be less than or equal to 20.0 percent. Otherwise, a calibration curve or a non-linear calibration (polynomial equation) must be used.

Linear calibration using least squares regression – If the RSD is greater than 20%, or if the analyst so chooses, linearity through the origin cannot be assumed and a linear regression of response verses concentration equation that does not pass through the origin may be used. The instrument response is dependent variable (y) and the concentration is the independent variable (x). The regression will produce the slope and intercept for a linear equation (y=mx+b) where y is the peak area, m is the slope, x is the concentration and b is the intercept. The origin is not forced through zero and do not use the origin as the sixth calibration point. The regression calculation will result in the correlation coefficient – r –, which is a measure of the "goodness of fit". A value of 1.00 is perfect, and for quantitative purposes, r must be greater than or equal to 0.99.

Non-linear calibration – if other approaches don't meet criteria, no more than third order non-linear may be used. First order (linear) requires five standards, second order (quadratic) model requires six standards and third order requires seven standards. The "goodness of fit" of the polynomial equation is evaluated by the weighted coefficient of the determination (COD), which must be greater than 0.99.

Calibration verification using a mid-point calibration standard is performed after the analysis of every 10 samples. The calibration factor should not exceed ± 15% difference or drift, where %D is percent difference when performing the average response factor calibration and percent drift when using a regression calibration. If the %D of target analytes is greater than 15%, the calibration may be acceptable if the mean of the %Ds for all analytes is less than or equal to 15%. This approach will lead to greater uncertainty for those analytes for which the %D is greater than 15%. Otherwise, a new calibration must be performed.

Tentative identification of analytes occurs when a peak in the sample extract falls within the retention time window. Each identification must be confirmed using either a second dissimilar GC column or another technique (GC/MS). The agreement between concentrations should be less than 40% RPD. The higher of the two concentrations should be reported. If one result is significantly higher, check for overlapping peaks and baseline. If no problems are found, report the higher result and note in the case narrative.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass in nanograms

Concentration (µg/L) = Area analyte * Conc IS * Dilution factor * Vol of extract (µl)
/Area IS*mean CF (IC) *Vol sample extracted (ml) * 1000

Concentration (µg/Kg) = Area analyte * Conc IS * Dilution factor * Vol of extract injected (µl) /Area IS*mean CF (IC) *weight sample (g) * 1000

Check for transcription/calculation errors for calibration factors, %RSDs, and %Ds. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

7.1 Validation Action:

a - If retention time windows, are not calculated correctly, contact laboratory for corrected resubmission of the data package with corrected windows; use the corrected values for all evaluations.

b - If the sample concentration exceeds the linearity of the calibration curve, and the sample is not properly diluted and re-analyzed, flag the positive results "J".

c - If the standard concentration criteria are not met, flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

d - If the %RSD criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

e - If the %D criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

f - Do all standard retention times fall within the windows established during the Initial Calibration?

ACTION: If no, all samples in the entire analytical sequence are potentially affected. Check to see if the chromatograms contain peaks within an expanded window surrounding the expected retention times. If no peaks are found and the surrogates are visible, non-detects are valid. If peaks are present and cannot be identified through pattern recognition or using a revised RT window, qualify all positive results "JN" and non-detects as unusable (R).). If the retention time windows are grossly exceeded, this should be noted in the data validation report. Retention time windows should be checked for calculation errors and corrections should be requested from the laboratory.

g – Was the correct analytical sequence used for calibration verification analyses?

ACTION: If no flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

h - If two columns were used to report sample results, only qualify if calibration excursions are detected on both columns.

7.2 List below all initial calibrations and calibration verifications and list samples qualified due to calibration excursions.

INSTRUMENT ID:

Column ID	Calibration ID - Date/Time	Analyte	Excursion retention time %RSD	Samples affected (client/lab ID) and action

8.0 FIELD DUPLICATE ANALYSIS

Note for Region V, field duplicates are not used to qualify samples; the RPDs are documented in the data validation report.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD

9.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION AND REPORTED DETECTION LIMITS

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present). The objective is to ensure that the reported quantitative results and contract required quantitation limits (CRQLs) are accurate

Retention time windows are established for compound identification. Three injections of analyte single and multi-component standards over a 72 hour period. The width of the retention time window is ± 3 times the standard deviation of the mean absolute retention time established during the 72 hour period. The absolute retention time for each analyte and surrogate from the calibration verification standard or the mid-point initial calibration standard establishes the center of the retention time window. Each analyte in each standard must fall within its retention time window.
Either second column or GC/MS analysis is performed for confirmation.
Tentative identification of analytes occurs when a peak in the sample extract falls within the retention time window. Each identification must be confirmed using either a second dissimilar GC column or another technique (GC/MS). The agreement between concentrations should be less than 40% RPD. The higher of the two concentrations should be reported. If one result is significantly higher, check for overlapping peaks and baseline. If no problems are found, report the higher result and note in the case narrative. The retention times of both of the surrogates, matrix spikes, and reported compounds in each sample must be within the calculated retention time windows on both columns.

When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract should use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses. Chromatograms should display herbicides detected in the sample at less than full scale.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass in nanograms

Concentration (µg/L) = Area analyte * Conc IS * Dilution factor * Vol of extract (µl)
/Area IS*mean CF (IC) *Vol sample extracted (ml) * 1000
Concentration (µg/Kg) = Area analyte * Conc IS * Dilution factor * Vol of extract injected (µl)
/Area IS*mean CF (IC) *weight sample (g) * 1000

Validation Action:
Confirm reported detected analytes by comparing the sample chromatograms to the tabulated results and verifying peak measurements and retention times. Confirm reported non-detected analytes by a review of the sample chromatograms. Check the associated blank data for potential interferences (to evaluate sample data for false positives) and check the calibration data for adequate retention time windows (to evaluate sample data for false positives and
false negatives).

9.1 If the retention time criteria for both columns were not met, or if interference is present, all target compounds that are reported detected should be considered non-detected.
a. If the misidentified peak was sufficiently outside the retention time window, then the reported values may be a false positive and should be replaced with the sample CRQL value.
b. If the misidentified peak poses an interference with potential detection of a target peak, then the reported value should be considered and qualified as unusable (R).

9.2 If the data reviewer identifies a peak in both GC column analyses that falls within the appropriate retention time

windows, but was reported as a non-detect, then the compound may be a false negative. Professional judgement should be used to decide if the compound should be included. All conclusions made regarding target compound identification should be included in the data review narrative.

9.3 Quantitation limits affected by large, off-scale peaks should be qualified as unusable (R). If the interference is on-scale, the reviewer can provide an approximated quantitation limit (UJ) for each affected compound.

9.4 Results are checked for agreement between quantitative results obtained on the initial and confirmation analysis. The agreement between concentrations should be less than 40% RPD. The higher of the two concentrations should be reported. If one result is significantly higher, check for overlapping peaks and baseline. If no problems are found, report the higher result and note in the case narrative. If an interfering compound is indicated, professional judgement must be used to determine how best to report, and if necessary, qualify the data.

9.5 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other_____?
Actions: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement in quality data.

9.6 Were samples reanalyzed at the appropriate dilution, when saturation occurred or when concentrations exceed linear range of the calibration curve?
Note: When sample dilution is performed, the laboratory typically reports two sets of sample data, diluted sample with responses within linear range and undiluted sample (least diluted sample is reported if two sets of dilutions were performed).
Action: Sample results quantitated with responses that exceed calibration range are approximated (J). In addition depending on data quality objectives of the project reanalysis of diluted extract may be required. Review resolutions in the narrative report.

9.7 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions and for soils, sample moisture?
Actions: If no and errors are large, request resubmittal of data package.

9.8 Were compounds detected at concentrations below CRQL (or PQL) reported and qualified with a "J"?
Actions: If no, note in the data validation report.

Document which sample analyses were reviewed and indicate frequency of raw data review, approximately 10% of data should be verified through raw data review. Show calculation below:

ADDITIONAL NOTES

O'Brien & Gere Engineers Data Validation Form
USEPA Method 8151A Chlorinated Herbicides
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ PARTIAL VALIDATION
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8151A	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 3520C 3550B 8151A	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses for Pesticides by USEPA SW-846 Method 8151A

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8151A. (National Functional Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is not reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR HERBICIDES ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues with sample receipt or condition of samples.

1.2 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.3 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.4 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.5 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method 8151A: Aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Validation Actions:

a. If extraction holding times are exceeded, associated sample results are flagged as estimated (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of target and/or non-target analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment. Laboratory generated control limits are used to evaluate the recoveries. For 8151A, 2,4-dichlorophenylacetic acid (DCAA) at a concentration of 0.5 mg/L is used.

3.1 Was the surrogate evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Validation Actions: Qualification of data is necessary if the surrogate is out of control limits. If interferences are present, qualification of sample results due to surrogate excursions is not performed.

a. If %recovery is <10%, and no interference is present, flag positive results as estimated (J) and reject detection limits (R).
b. If %recovery is 10% to lower control limit, and no interference is present, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, and no interference is present, flag positive results as estimated (J).
d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.
e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with method requirements.
f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
g. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.2 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:

DCAA – 2,4-dichlorophenylacetic acid

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

Validation Actions: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). However, if the percent recovery of the compound is above the upper limit but less than 100%, the unspiked sample is not qualified.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and nondetected results are approximated (UJ).
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.3 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.2 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed for 8151A analysis to ensure that the GC system and solvents used are free of contamination. The method blank should be carried through all stages of sample preparation and measurement.

Note for Region V, no "B" flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V, equipment blanks are not used to qualify samples; the detected contaminants are documented in the data validation report.
6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

Actions levels are calculated at 5x blank (method) value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with based upon a comparison with the associated blank having the highest concentration of a contaminant. Instrument blanks should be analyzed after high concentrations; otherwise carryover may be suspected.

Validation Actions:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.4 List all blanks and samples qualified due to blank contamination.
Note for Region V, equipment blanks are not used to qualify samples; the detected contaminants are documented in the data validation report.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 FIELD DUPLICATE ANALYSIS

Note for Region V, field duplicates are not used to qualify samples; the RPDs are documented in the data validation report.

7.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD

Section 5

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Modified Method 680 Polychlorinated Biphenyl (PCB)/SIM/GC/MS – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Modified Method 680 Polychlorinated Biphenyl (PCB)/SIM/GC/MS – Partial Validation

O'Brien & Gere Engineers Data Validation Form
USEPA Modified Method 680 Polychlorinated Biphenyl (PCB) SIM/GC/MS
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ FULL V ALIDATION
Method reference: USEPA. 1985. Determination of Pesticides and PCBs in Water and Soil/Sediment by GC/MS. Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 680	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 680	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent usability = Usable analyses (total analyses – rejected analyses) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent rejected	Percent usability

Data Validation Forms
For Analyses of PCBs USEPA Modified Method 680

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois and
- USEPA. 1994. *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012, Washington D.C.
- USEPA. 1985. Determination of Pesticides and PCBs in Water and Soil/Sediment by GC/MS, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio.

(National Functional Guidelines and Region V apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR PCB ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of PCB data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, µg/L for waters and µg/kg for soils?

1.4 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.5 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.6 Was appropriate clean up used (Gel permeation chromatography [GPC]) for high concentrations of non-volatiles – lipids, resins, polymers, acid, sulfur for high levels of sulfur?

1.7 Were any of the samples diluted? Were dilutions performed when necessary? Note if samples were combined due to dilutions.

1.8 Were raw data to support analyses and QC operations present and complete?

ACTIONS: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.9 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms, etc).

1.10 Were equipment blanks, MS/MSD, and field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Validation Method 680: Aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

Validation Actions:

a. If extraction holding times are exceeded, associated sample results are flagged as estimated (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and non-detected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or re-analysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries.
For 680, 13C12- decachlorobiphenyl at 1.0 µg is spiked prior to sample extraction.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Percent recovery = conc found/conc spiked * 100

Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

Validation Actions: Qualification of data is necessary if the surrogate is out of control limits. If interferences are present, no qualification of samples is performed.

a. If % recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).
b. If % recovery is 10% to lower control limit, flag associated sample results and detection limits as estimated (UJ,J).
c. If % recovery is > upper control limit, flag positive results as estimated (J).
b. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Reject associated sample data if surrogates were not evaluated. Use professional judgement in qualifying sample data if the incorrect concentrations were used.
c. If surrogate recovery is outside of criteria, the lab should perform a re-analysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If a re-analysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.
d. If surrogate recoveries exceeded criteria in the re-analysis, the laboratory is required to report both sets of sample data. Validate both sets of sample results and qualify data.

3.2 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	Percent Recovery [control limits]	Action
Note: 13C12DCBP – 13C12-decachlorobiphenyl			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically 1 in 20)?

4.1.1 Were laboratory batch QC performed?

For 680 – The matrix spiking solution contains one PCB congener of each chlorination level except for the nonachlorobiphenyls. The solution is prepared at the following concentrations in acetone and 1.0mL of this solution is spiked into all lab spikes and matrix spikes:

COMPOUND	COMPOUND / CONCENTRATION (µg/mL)
2-Chlorobiphenyl	2.0
2,3-Dichlorobiphenyl	2.0
2,4,5-Trichlorobiphenyl	2.0
2,2',4,6-Tetrachlorobiphenyl	4.0
2,2',3,4,5'-Pentachlorobiphenyl	4.0
2,2',4,4',5,6'-Hexachlorobiphenyl	4.0
2,2',3,4',5,6,6'-Heptachlorobiphenyl	6.0
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	6.0
Decachlorobiphenyl	10

If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections

Validation Actions: Qualification is limited to the unspiked sample only.
RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are rejected (R).
b. If **both** MS/MSD recoveries are > upper control limits, detected results are approximated (J). However, if the percent recovery of the compound is above the upper acceptance limit, but less than 100%, the unspiked sample results are not qualified.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and non-detected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and non-detected results are qualified as approximated (UJ).
e. If MS/MSDs were not analyzed, contact laboratory for explanation and describe problems/resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.2 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	Percent Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the re-analysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries are greater than control limits, approximate detected results (J).
b. If LCS recoveries are less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries are <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs are not analyzed, contact laboratory for explanation and describe problems/resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	Percent Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSIS

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. A method blank is analyzed for 680 analysis to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contamination.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V, the equipment blank is not used to qualify sample results; the detected contaminants are documented in the data validation report.
6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of 1 per 20 field samples.

Actions levels are calculated at 5x blank (method) value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.
Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected.

Validation Actions:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.3 List all blanks and samples qualified due to blank contamination.
Note for Region V, the equipment blank is not used to qualify sample results; the detected contaminants are documented in the data validation report.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 GC/MS TUNING AND WINDOW-DEFINING CRITERIA

Tuning and performance criteria are established to verify GC/MS performance.

For 680 - Twenty nanograms of DFTPP are analyzed at the beginning of each 12-hour clock as a check on the "tune" of the mass spectrometer. The DFTPP analysis is performed using scan analysis and the same tune parameters are used for the SIM analysis of the calibration standards and samples, using a 1µL aliquot of the 10ng/µL solution of DFTPP column evaluation standard and p,p'-DDT (4,4'-DDT), at the same temperature program that is used for SIM analysis of the calibration standards, samples, and QC samples.
For the evaluation:
a - The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.
b - The spectrum of the DFTPP must meet the criteria listed below.
c - Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.
NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, etc. If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

DFTPP Criteria for Method 680

m/z	Ion Abundance Criteria :
127	40-60% of mass 198
197	<1.0% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass443
442	>40% of mass 198
443	17-23% of mass 442

Window-Defining Solution and SIM Parameters
One µL of the window-defining solutions are analyzed in the scan mode from 45amu to 500amu at > 1 scan per second. The same temperature program that will be used for the SIM analysis of PCBs is used. The window-defining solutions may be analyzed separately or may be combined into a single solution. The retention times of the first and last eluting congeners at each level of chlorination are determined.
The SIM parameters are set as follows.
-Begin data acquisition with ion set #1 before the elution of PCB congener #1. Stop the acquisition of ion set #1 and begin acquisition of ion set #2 approximately 10 seconds before the elution of PCB congener #104.
-Stop the acquisition of ion set #2 and begin the acquisition of ion set #3 approximately 10 seconds after the elution of PCB congener #77.
-Stop the acquisition of ion set #3 and begin the acquisition of ion set #4 approximately 10 seconds after the elution of 4,4'-DDT. (the retention time of 4,4'-DDT is determined from the scan analysis of the DFTPP solution that is analyzed at the beginning of each 12-hour clock.).
-Stop the acquisition of ion set #4 and begin the acquisition of ion set #5 approximately 10 seconds before the elution of PCB congener #208.

7.1 Were GC/MS tuning performances for DFTPP analyzed for every twelve hours of sample analysis for each GC/MS instrument used?
7.2 Have the ion abundance criteria documented by the method been met for each tune?
7.3 Check for transcription/calculation errors. If errors are present briefly summarize necessary changes.
7.4 Are the spectra of the mass calibration acceptable?
7.5 Was the tune performance standard injected at the beginning of the analytical sequence and were all the samples analyzed within the 12-hour clock?

Validation Actions:

a. If tuning has not been done, reject (R) associated sample data and contact laboratory for explanation. Discuss in data completeness section in the data validation report.

b. If no for 7.2, 7.4, or 7.5 reject associated sample results.

Some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/199 and 442/443 are critical. These ratios are based on the natural abundances of carbon 12 and carbon 13 and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of the resolution adjustment and are very important. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. For instance, if m/z 275 has 40% relative abundance (criteria: 10.0-30.0%) and other criteria are met, then the deficiency is minor. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance for m/z 365 is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 0.75% minimum abundance criteria, the deficiency is not as serious.

7.5 List all tunes and samples qualified due to tune excursions.

INSTRUMENT ID:

Unique Tune ID	Date/Time	Comments	Tune Met	Samples affected (client/lab ID) and action

8.0 GC/MS INITIAL CALIBRATION

Calibration criteria has been established to verify that GC/MS is capable of producing acceptable quantitative data. All target compounds must have corresponding initial and continuing calibrations.

After the SIM windows are established and verified and the DFTPP criteria have been met, the initial calibration standards are analyzed. Note that a single PCB congener of each chlorination level is used for calibration and quantitation. Decachlorobiphenyl is used to quantify nonachlorobiphenyls. The standards are prepared as listed in the following table. The lowest calibration standard should be at the RL and the rest of the standards will define the working range. The injection volume must be the same for the calibration standards and all sample extracts. The routine volume is 1µL. If the %RSD of each target compound is less than or equal to 20%, the average response factor can be used for quantitation of samples. If the %RSD of the target compound is greater than 20%, the curve should be evaluated for errors and one or more standards re-analyzed. Corrective action is required until the %RSD of each target is less than 20%.

In addition to meeting the calibration criteria, the following performance criteria must also be met for the mid-level standard:
a -Mass abundance ratios of all calibration congeners within acceptance range
b - Baseline separation of PCB congener #87 from congeners #154 and #77
c - Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241
d - Decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498

Calibration Standards

Calibration Congener – calibration standard concentrations	
2-chlorobiphenyl (1)	- 0.10 0.50 1.0 2.0 5.0
2,3-dichlorobiphenyl(5)	- 0.10 0.50 1.0 2.0 5.0
2,4,5-trichlorobiphenyl(29)	- 0.10 0.50 1.0 2.0 5.0
2,2',4,6-tetrachlorobiphenyl(50)	- 0.20 1.0 2.0 4.0 10
2,2',3,4,5'-Pentachlorobiphenyl (87)	- 0.20 1.0 2.0 4.0 10
2,2',4,4',5,6'-hexachlorobiphenyl(154)	- 0.20 1.0 2.0 4.0 10
2,2',3,4',5,6,6'-heptachlorobiphenyl(188)	- 0.30 1.5 3.0 6.0 15
2,2',3,3',4,5,5',6,6'-octachlorobiphenyl(200)	- 0.30 1.5 3.0 6.0 15
Decachlorobiphenyl	- 0.50 2.5 5.0 10 25
Retention Time Congeners	
3,3',4,4-tetrachlorobiphenyl(77)	- 0.20 1.0 2.0 4.0 10
2,2',4,6,6'-Pentachlorobiphenyl (104)	- 0.20 1.0 2.0 4.0 10
2,2',3,3',4,5,5',6,7'-nonachlorobiphenyl(208)	- 0.40 2.0 4.0 8.0 20
Surrogate	
13C12-Decachlorobiphenyl	- 0.50 2.5 5.0 10 25
Internal Standards	
Phenathrene-d10	- 0.75 0.75 0.75 0.75 0.75
Chrysene-d12	- 0.75 0.75 0.75 0.75 0.75

Quantitation and Interference Check Ions

PCB Isomer Group	Quant ION	Confirmation ION	Expected Ratio(a)	Acceptable Ratio(a)	M-70 Confirmation	ION Interference Check ION M+70	Interference Check ION M+35
CL-1	188	190	3.0	2.5-3.5	152	256	222
CL-2	222	224	1.5	1.3-1.7	152	292	256
CL-3	256	258	1.0	0.8-1.2	186	326	290
CL-4	292	290	1.3	1.1-1.5	220	360	326
CL-5	326	324	1.6	1.4-1.8	354	394	360
CL-6	360	362	2.1	1.0-1.4	288	430	394
CL-7	394	396	1.0	0.8-1.2	322	464	430
CL-8	430	428	1.1	0.9-1.3	356	498	464
CL-9	464	466	1.3	1.1-1.5	390	-	498
CL-10	498	500	1.1	0.9-1.3	424	-	-
Chrysene-d12	240	241	5.1	4.3-5.9	-	-	-
Phenathrene-d10	188	189	6.6	6.0-7.2	-	-	-
13C12-DCB	510	512	-	-	-	-	-

(a) ratio of quantitation ion to confirmation ion

Corrections for Interference of PCB Containing Two Additional Chlorines

PCB Isomer Group	Quantitation ION	Confirmation ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUANTITATION ION Area	Percent Ion area to be subtracted from CONFIRMATION ION Area
CL-3	256	258	254	99	33
CL-4	292	290	288	65	131
CL-5	326	324	322	108	164
CL-6	360	362	356	161	71
CL-7	394	396	390	225	123

Corrections for Interference of PCB Containing One Additional Chlorine

PCB Isomer Group	Quantitation ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUANTITATION ION Area
CL-2	222	221	13.5
CL-3	256	255	13.5
CL-4	292	289	17.4
CL-5	326	323	22.0
CL-6	360	357	26.5
CL-7	394	391	30.9
CL-8	430	425	40.0

8.1 Were initial calibrations performed at the required concentrations prior to sample analysis, whenever GC/MS system is modified, and whenever continuing calibration criteria are exceeded?
8.2 Did the initial calibration meet criteria?
8.3 Were the performance criteria met for the mid-level standard?

Validation Actions:

a. If initial calibration data can not provided, reject associated sample data (R).
b. If RSD exceeds criteria, approximate detected and non-detected results (UJ, J).
c. If performance criteria exceed criteria, approximate detected and non-detected results (UJ, J).

8.2 Check for transcription/calculation errors; check a minimum of one compound/internal standard to verify that calibration factors have been calculated correctly. Show calculation below.

8.3 List below all initial calibrations and samples qualified due to initial calibration excursions.

INSTRUMENT ID:

Unique IC ID	Date	Compound	Excursion: Percent RSP Performance criteria	Action	Samples Affected (client/lab ID)

9.0 CONTINUING CALIBRATION

The initial calibration is verified once every 12 hours.

Samples are analyzed only after the DFTPP criteria and the calibration acceptance criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the DFTPP and a mid-level calibration standard prior to the analysis of the samples and after the samples by the analysis and evaluation of a mid-level standard. If the percent difference is less than or equal to 20% for each target compound, the initial calibration is verified. If the continuing calibration criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the analysis of the continuing calibration standard must be repeated. The analyst must be aware of the 12-hour clock-DFTPP criteria, which must be met prior to the analysis of the calibration standards. If the continuing calibration standard repeatedly fails the calibration verification criteria, the initial calibration curve must be re-analyzed and reevaluated.

The initial calibration performance criteria must also be met prior to the analysis of samples.

9.1 Were continuing calibration standards analyzed for each twelve hours of sample analysis for each GC/MS?
9.2 Did the continuing calibration verification meet criteria?
9.3 Were the performance criteria met?

Validation Actions:

a. If no, contact laboratory for explanation and review in data completeness section. Immediately contact Project Manager if continuing calibration data can not be provided.
c. If %D exceeds criteria, approximate detected and non-detected results (UJ, J).
d. If performance criteria exceed criteria, approximate detected and non-detected results (UJ, J).

9.2 Check for transcription/calculation errors; check a minimum of one compound/internal standard to verify that calibration factors have been calculated correctly, using the specified internal standard.

9.3 List below all continuing calibrations and samples qualified due to continuing calibration excursions.

INSTRUMENT ID:

Unique CC ID	Date	Compound	Excursion: Percent D Performance criteria	Action	Samples Affected (client and lab ID)

10.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

For 680, the internal standard in all standards and samples are evaluated. The area in the continuing calibration verification must be within 30% of the previous continuing calibration verification and within 50% of the initial calibration. Areas in samples should be evaluated for gross error. The area should be within 30% of the previous continuing calibration verification and within 50% of the initial calibration. The ion abundance criteria must be met. The RT must be within the acceptance criteria. If the internal standard retention times have changed significantly or the peaks cannot be located, stop the analysis and correct the problem. Re-analyze any associated samples.

10.1 Were internal standard areas of samples and continuing calibration within recovery and retention time criteria?

Note: The laboratory is required to re-analyze samples when internal standard criteria are not met.

Validation Actions:

a. If area count is above the limit, approximate (J) detected results.
b. If area count is below limits, approximate detected and nondetected results (UJ,J).
c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R), and approximate detected results (J).
d. If the retention times have significantly changed from the nearest calibration standard, the associated detection limits are rejected (R).

10.2 Is the ion abundance criteria met?

Validation Action:
Approximate detected and nondetected results (UJ,J) for compounds.

10.3 Were samples re-analyzed when internal standard criteria were exceeded?

Validation Action: Document in the narrative report that the laboratory was not in compliance with analytical method requirements.

If yes, and internal standard areas remain outside criteria, validate both sets of sample data with respect to above actions.

10.4 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Action

11.0 FIELD DUPLICATE ANALYSIS

Note for Region V, the field blank is not used to qualify sample results; the RPDs are documented in the data validation report.

11.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below the results; RPDs are documented in the data validation report.

Duplicate IDs	Compound	RPD

12.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION AND REPORTED DETECTION LIMITS

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

The objective of the criteria for qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).
For quantitation evaluation, the objective is to ensure that the reported quantitation results and the detection limits are accurate.

A peak is tentatively identified as a PCB if:
-The peak falls within the retention time range bordered by the first and last eluting isomer of that chlorination level.
-The ratio of the quantitation and confirmation ions are present and the area ratios fall within the acceptance criteria. The scans must maximize within one scan of each other.

The data are examined for the presence of a coeluting PCB of higher chlorination if both ions and the M-70 ions are present and the ratio does fall within the acceptance limits.
-The areas for the quantitation and confirmation ions must be greater than three times the background noise and must fall within the working range of the calibration curve (must not saturate the detector).
-At least one ion in the M-70 cluster must be present.

Each PCB candidate in the Cl-3 to Cl-7 range is examined for the presence of coeluting PCBs containing one or two additional chlorines. An intense M+35 ion at the retention time may indicate a PCB with one additional chlorine and the presence of an intense M+70 would indicate a co-eluting PCB containing two additional chlorines. Correct for the interfering ion(s) using appropriate tables. For example, if a Cl-7-PCB and a Cl-5-PCB coelute, the Cl-7-PCB will contribute to the quantitation and confirmation ions for the Cl-5-PCB. Cl-7-PCB produces a cluster of three ions by the loss of two chlorine-ions 322,324, and 326. Two of these ions-324 and 326-are also ions contained in the molecular ion cluster of Cl-5-PCB. To determine the ion 326 and 324 areas produced only by the Cl-5-PCB, calculate the contribution to each and subtract it from the measured areas. See tables for the percentage of the interference peak to subtract from the quantitation and confirmation ions. In this example, 164% of the area measured for ion 322 should be subtracted from the area measured for ion 324 and 108% of the area measured for ion 322 should be subtracted from ion 326. A coeluting PCB with one more chlorine will affect only the quantitation ion. The interference from a coeluting PCB containing one more chlorine, due to the natural abundance of 13C12, is small and can usually be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of a another PCB containing one more chlorine.

Sample calculation:

$$\text{Concentration } (\mu g/L) = \frac{\text{Area analyte} * \text{Conc IS} * \text{Dilution factor} * \text{Vol of extract } (\mu l)}{\text{Area IS} * \text{RRF average} * \text{Volume sample extracted (ml)} * 1000}$$

$$\text{Concentration } (\mu g/Kg) = \frac{\text{Area analyte} * \text{Conc IS} * \text{Dilution factor} * \text{Vol of extract injected } (\mu l)}{\text{Area IS} * \text{RRF average} * \text{weight sample (g)} * 1000}$$

12.1 Were the congeners within the retention time range?

12.2 Were the ion current responses for both quantitation and confirmation ions maximized within 1 scan?

12.3 Were the quantitation and confirmation ion abundance criteria met?

12.4 Were the areas for the quantitation and confirmation ions greater than three times the background noise?

12.5 Was at least one ion in the M-70 cluster present?

12.6 Were coeluting PCBs present and were they corrected for?

Actions: If no, for any of the above, positive and non-detected results are qualified as estimated (UJ,J).

12.7 Were samples re-analyzed at the appropriate dilution, when saturation occurred or when concentrations exceed linear range of the calibration curve?

Note: When sample dilution is performed, the laboratory typically reports two sets of sample data: the diluted sample with responses within linear range and the undiluted sample (least diluted sample is reported if two sets of dilutions were performed).

Action: Sample results quantitated with responses that exceed calibration range are approximated (J). Depending on data quality objectives of the project, re-analysis of diluted extract may be required. Review resolutions in the narrative report.

12.8 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions and for soils, sample moisture?

Actions: If no and errors are large, request resubmittal of data package.

12.9 List samples qualified due to identification excursions:

Sample ID (client/lab)	Compound	Excursion	Action

Document which sample analyses were reviewed and indicate frequency of raw data review. Approximately 10% of data should be verified through raw data review. Show calculation below:

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form
USEPA Modified Method 680 Polychlorinated Biphenyl (PCB) SIM/GC/MS
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Blanks:_____
Project: _____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ PARTIAL VALIDATION
Method reference: USEPA. 1985. Determination of Pesticides and PCBs in Water and Soil/Sediment by GC/MS, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 680	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 680	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent usability = Usable analyses (total analyses – rejected analyses) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent rejected	Percent usability

Data Validation Forms
For Analyses of PCBs USEPA Modified Method 680

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*. Chicago. Illinois and
- USEPA. 1994. *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. EPA-540/R-94/012. Washington D.C.
- USEPA. 1985. Determination of Pesticides and PCBs in Water and Soil/Sediment by GC/MS. Physical and Chemical Methods Branch. Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio.

(National Functional Guidelines and Region V apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is not reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR PCB ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues with sample receipt or condition of samples.

1.2 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.3 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.4 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.5 Were equipment blanks, MS/MSD, and field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Validation Method 680: Aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Validation Actions:

a. If extraction holding times are exceeded, associated sample results are flagged as estimated (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and non-detected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or re-analysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries.
For 680, 13C12- decachlorobiphenyl at 1.0 μg is spiked prior to sample extraction.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Validation Actions: Qualification of data is necessary if the surrogate is out of control limits. If interferences are present, no qualification of samples is performed.

a. If % recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).
b. If % recovery is 10% to lower control limit, flag associated sample results and detection limits as estimated (UJ,J).
c. If % recovery is > upper control limit, flag positive results as estimated (J).
b. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Reject associated sample data if surrogates were not evaluated. Use professional judgement in qualifying sample data if the incorrect concentrations were used.
c. If surrogate recovery is outside of criteria, the lab should perform a re-analysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If a re-analysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.
d. If surrogate recoveries exceeded criteria in the re-analysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data.

3.2 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	Percent Recovery [control limits]	Action
Note: 13C12DCBP – 13C12-decachlorobiphenyl			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically 1 in 20)?
4.2 Were laboratory batch QC performed?

Validation Actions: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are rejected (R).
b. If **both** MS/MSD recoveries are > upper control limits, detected results are approximated (J). However, if the percent recovery of the compound is above the upper acceptance limit, but less than 100%, the unspiked sample results are not qualified.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and non-detected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and non-detected results are qualified as approximated (UJ).
e. If MS/MSDs were not analyzed, contact laboratory for explanation and describe problems/resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.2 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	Percent Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the re-analysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries are greater than control limits, approximate detected results (J).
b. If LCS recoveries are less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries are <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs are not analyzed, contact laboratory for explanation and describe problems/resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.2 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	Percent Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSIS

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. A method blank is analyzed for 680 analysis to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contamination.

6.1 Were method blanks analyzed for each group of samples of similar matrix?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V, the equipment blank is not used to qualify sample results; the detected contaminants are documented in the data validation report.
6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of 1 per 20 field samples.

Actions levels are calculated at 5x blank (method) value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.
Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected.

Validation Actions:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.4 List all blanks and samples qualified due to blank contamination.
Note for Region V, the equipment blank is not used to qualify sample results; the detected contaminants are documented in the data validation report.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

For 680, the internal standard in all standards and samples are evaluated. The area in the continuing calibration verification must be within 30% of the previous continuing calibration verification and within 50% of the initial calibration. Areas in samples should be evaluated for gross error. The area should be within 30% of the previous continuing calibration verification and within 50% of the initial calibration. The ion abundance criteria must be met. The RT must be within the acceptance criteria. If the internal standard retention times have changed significantly or the peaks cannot be located, stop the analysis and correct the problem. Re-analyze any associated samples.

7.1 Were internal standard areas of samples and continuing calibration within recovery and retention time criteria?

Note: The laboratory is required to re-analyze samples when internal standard criteria are not met.

Validation Actions:

a. If area count is above the limit, approximate (J) detected results.
b. If area count is below limits, approximate detected and nondetected results (UJ,J).
c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R), and approximate detected results (J).
d. If the retention times have significantly changed from the nearest calibration standard, the associated detection limits are rejected (R).

7.2 Were samples re-analyzed when internal standard criteria were exceeded?

Validation Action: Document in the narrative report that the laboratory was not in compliance with analytical method requirements.

If yes, and internal standard areas remain outside criteria, validate both sets of sample data with respect to above actions.

7.3 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Action

8.0 FIELD DUPLICATE ANALYSIS

Note for Region V, the field blank is not used to qualify sample results; the RPDs are documented in the data validation report.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below the results; RPDs are documented in the data validation report.

Duplicate IDs	Compound	RPD

Section 6

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8015B TPH, Nonhalogenated Organics – DRO/GRO – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8015B TPH, Nonhalogenated Organics – DRO/GRO – Partial Validation

O'Brien & Gere Engineers Data Validation Form
USEPA Method 8015B TPH- Nonhalogenated Organics/DRO/GRO
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Banks:_____
Project:_____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ FULL VALIDATION
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8015B	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8015B	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses of TPH/DRO/GRO by USEPA SW-846 Method 8015B (GC/FID)

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data.* Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington. D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8015B. (National Functional Guidelines and Region V Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR TPH ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of TPH data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, ug/L for waters and ug/kg for soils?

1.4 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.5 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.6 Was appropriate sample preparation/sample introduction technique used?
For volatile organics (gasoline range organics –GRO): direct injection for azeotropic distillation (Method 5031), purge and trap for aqueous (Method 5030), purge and trap for solids, extraction of solid and oily waste (Method 5035), vacuum distillation for aqueous, solid or tissue (Method 5032), automated static headspace for solids (Method 5021)
For semivolatile organics (diesel range organics – DRO): separatory funnel (Method 3510), continuous liquid/liquid (Method 3520), Soxhlet (Method 3540), Automatic soxhlet (Method 3541), pressurized fluid (Method 3545), ultrasonic (Method 3550), supercritical fluid (Method 3560)

1.7 Was confirmation analysis performed (by GC or GC/MS)? (Required for single component analytes; not required for petroleum hydrocarbon analysis unless matrix interference is present)

1.8 Were any of the samples diluted? Were dilutions performed when necessary? Note if samples were combined due to dilutions.

1.9 Were raw data to support analyses and QC operations present and complete?

Actions: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.10 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.11 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of results based on holding of the same from the time of sample collection to the time of preparation or analysis.

2.1 Method 8015B: Volatile samples must be analyzed within 14 days of collection. Semivolatile aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

VALIDATION ACTIONS:

a. If extraction holding times are exceeded associated sample results are flagged as estimated (UJ, J).
b. If analysis holding times are exceeded detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than 2 times the criteria, nondetected sample results are rejected, (R), and detected sample results are approximated (J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries. Method 8015B did not recommend any surrogates to be used.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Percent recovery = conc found/conc spiked * 100

3.3 Were the retention times of both of the surrogates in standards, blanks and samples within the calculated retention time windows?

VALIDATION ACTIONS: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).
b. If %recovery is 10% to lower control limit, flag associated sample results and detection limits as estimated (UJ, J).
c. If %recovery is > upper control limit, flag positive results as estimated (J).
d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.
e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.
f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
g. If surrogate retention times in standards, samples, and blanks are outside of the retention time window, flag associated sample results and detection limits as estimated (UJ, J).
h. If interference was present, qualification of samples due to surrogate excursions is not performed.
i. If zero pesticide surrogate recovery is reported, the reviewer should examine the sample chromatogram to determine if the surrogate may be present, but slightly outside its retention time window. If this is the case, in addition to assessing surrogate recovery for quantitative bias, the overriding consideration is to investigate the qualitative validity of the analysis. If the surrogate is not present, qualify all nondetected target compounds as unusable (R).

j. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.4 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action
Note: Surrogates -			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations). whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

Validation Actions: Qualification is limited to the unspiked sample only.
RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and detection limits (UJ).
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.2 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).

b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ, J).

c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).

d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. A method blank is analyzed to ensure that the GC system and solvents used are free of contamination.
Note for Region V, no "B" flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix extracted and analyzed?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.
6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

There may be instances when little or no contamination was present in the associated blanks, but qualification of the sample was deemed necessary. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. However, if the reviewer determines that the contamination is from a source other than the sample, the data should be qualified. In this case, the "5x" rule does not apply; the sample value should be reported as a non-detected target compound, "U". An explanation of the rationale for this determination should be provided in the validation report.

If gross contamination exists (e.g., saturated peaks, "hump-o-grams", "junk" peaks), all affected compounds in the associated samples should be qualified as unusable (R), due to interference. This should be noted in the data validation, and as an action item if the contamination is suspected of having an effect on the sample results.

If inordinate amounts of target or non-target compounds are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted for action.

If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification(s), and if so, detected compound results should be qualified.

Actions levels are calculated at 5x blank value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.
Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected.

VALIDATION ACTIONS:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.3 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 GC INITIAL CALIBRATION AND CALIBRATION VERIFICATION

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide compounds. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence and of producing a linear calibration curve.

Gasoline range organics (GRO) correspond to the range of alkanes form C6 to C10 and Diesel range organics (DRO) correspond to the range of alkanes from C10 to C28. Calibration standards should be prepared at a minimum of five concentrations that correspond to the expected range of concentrations in the samples and should bracket the linear range of the detector. One standard should be at or below the reporting limit.

Single component analytes are identified based on retention times. GROs and DROs are identified based on the ranges of retention times for components in each type of fuel. The retention time for GROs and DROs are established during the initial calibration. For GROs, two gasoline components (2-methylpentane and 1,2,4-trimethylbenzene) are used. For DROs, C10 and C28 alkanes are used. The retention time is calculated based on the lower limit of the retention time window for the first eluting component and the upper limit of the window for the last eluting component.

For Retention time windows for single component analytes, three injections of analyte single component standards over a 72-hour period. The width of the retention time window is ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. The absolute retention time for each analyte and surrogate from the calibration verification standard or the mid-point initial calibration standard establishes the center of the retention time window. Each analyte in each standard must fall within its retention time window.

Internal standards (hexafluoro-2-propanol, hexafluoro-2-methyl-2-propanol, and 2-chloroacrylonitrile for non-purgable volatiles) (2-chloroacylonitrile, hexafluoro-2-propanol, and hexafluror-2-methyl-2-propanol for azeotropic distillation) may be used for internal calibration. External standard calibration is used for DRO and GRO. The response used for calibration must represent the entire area of chromatogram within the retention time range for the DRO or GRO, including the unresolved complex mixture that lies below the individual peaks. The calibration should be performed using the specific fuel that is at the site.

The Percent Relative Standard Deviation (%RSD) of the calibration factors for each of the single component compounds and fuel types in the initial calibration on both columns must be less than or equal to 20.0 percent. Otherwise, a calibration curve or a non-linear calibration (polynomial equation) must be used.

Linear calibration using least squares regression – If the RSD is greater than 20%, or if the analyst so chooses, linearity through the origin cannot be assumed and a linear regression of response verses concentration equation that does not pass through the origin may be used. The instrument response is dependent variable (y) and the concentration is the independent variable (x). The regression will produce the slope and intercept for a linear equation ($y=mx+b$) where y is the peak area, m is the slope, x is the concentration and b is the intercept. The origin is not forced through zero and does not use the origin as the sixth calibration point. The regression calculation will result in the correlation coefficient – r –, which is a measure of the "goodness of fit". A value of 1.00 is perfect, and for quantitative purposes, r must be greater than or equal to 0.99.

Non-linear calibration – if other approaches don't meet criteria, no more than third order non-linear may be used. First order (linear) requires five standards, second order (quadratic) model requires six standards and third order requires seven standards. The "goodness of fit" of the polynomial equation is evaluated by the weighted coefficient of the determination (COD), which must be greater than 0.99.

Calibration verification is performed every 12-hour shift for all target analytes. Additional calibration standards should be injected at intervals throughout the 12-hour shift. The calibration standard should be mid-concentration that contains all single component target analytes. Verification of fuel is accomplished by the measurement of fuel standards and the hydrocarbon retention time standard. The calibration factor should not exceed ± 15% difference or drift, where %D is percent difference when performing the average response factor calibration and percent drift when using a regression calibration. The %D for azeotropic distillation samples is 20%. Otherwise, corrective action must be performed. All target analytes and surrogates or n-alkanes in the calibration verification standard must fall within the retention time windows. Otherwise, corrective action must be performed.

The analytical sequence starts with the calibration verification, followed by sample extracts. Additional calibration verifications are suggested throughout the 12-hour shift and are required at the end of the sequence.

Confirmation is required for single component analytes but is not required for petroleum hydrocarbon analysis unless matrix interference is present. The early eluting compounds in fuels are the most volatile and the most likely to have weathered. The most highly volatile fraction of gasoline constitutes 50% of the total peak area of a gasoline chromatogram. This fraction is least likely to be present in an environmental

sample or present in a low concentration in relation to the remainder of a gasoline chromatogram.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass injected in nanograms
CF fuel= total peak area within retention time range/ analyte mass injected in nanograms

Concentration (μg/L) = Area analyte * Conc IS * Dilution factor * Vol of extract (μl)
/Area IS*mean CF (IC) *Vol sample extracted (ml) * 1000
Concentration (μg/Kg) = Area analyte * Conc IS * Dilution factor * Vol of extract injected (μl)
/Area IS*mean CF (IC) *weight sample (g) * 1000

Check for transcription/calculation errors for calibration factors, %RSDs, and %Ds. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

7.1 VALIDATION ACTION:
a - If retention time windows, are not calculated correctly, contact laboratory for corrected resubmission of the data package with corrected windows; use the corrected values for all evaluations.
b - If the sample concentration exceeds the linearity of the calibration curve, and the sample is not properly diluted and re-analyzed, flag the positive results "J".
c - If the standard concentration criteria are not met, flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".
d - If the %RSD criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".
e - If the %D criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".
f - Do all standard retention times fall within the windows established during the Initial Calibration?
ACTION: If no, all samples in the entire analytical sequence are potentially affected. For single component analytes, check to see if the chromatograms contain peaks within an expanded window surrounding the expected retention times. If no peaks are found and the surrogates are visible, non-detects are valid. If peaks are present and cannot be identified through pattern recognition or using a revised RT window, qualify all positive results "JN" and non-detects as unusable (R).
g – Was the correct analytical sequence used for analyses?
ACTION: If no flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

7.2 List below all initial calibrations and calibration verifications and list samples qualified due to calibration excursions.

INSTRUMENT ID:

Column ID	Calibration ID - Date/Time	Analyte	Excursion retention time %RSD	Samples affected (client/lab ID) and action

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

8.2 Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

9.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION AND REPORTED DETECTION LIMITS

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present).

Gasoline range organics (GRO) correspond to the range of alkanes from C6 to C10 and Diesel range organics (DRO) correspond to the range of alkanes from C10 to C28. Single component analytes are identified based on retention times. GROs and DROs are identified based on the ranges of retention times for components in each type of fuel. The retention time for GROs and DROs are established during the initial calibration. For GROs, two gasoline components (2-methylpentane and 1,2,4-trimethylbenzene) are used. For DROs, C10 and C28 alkanes are used. The retention time is calculated based on the lower limit of the retention time window for the first eluting component and the upper limit of the window for the last eluting component.
For Retention time windows for single component analytes, three injections of analyte single component standards over a 72-hour period. The width of the retention time window is ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. The absolute retention time for each analyte and surrogate from the calibration verification standard or the mid-point initial calibration standard establishes the center of the retention time window. Each analyte in each standard must fall within its retention time window.

The analytical sequence starts with the calibration verification, followed by sample extracts. Additional calibration verifications are suggested throughout the 12-hour shift and are required at the end of the sequence.

Confirmation is required for single component analytes but is not required for petroleum hydrocarbon analysis unless matrix interference is present. The early eluting compounds in fuels are the most volatile and the most likely to have weathered . The most highly volatile fraction of gasoline constitutes 50% of the total peak area of a gasoline chromatogram. This fraction is least likely to be present in an environmental sample or present in a low concentration in relation to the remainder of a gasoline chromatogram.

Fuels contain many components that are not chromatographically resolved, which results in a "hump" in the chromatogram that is characteristic of fuels. The resolved peaks are important for identification but the unresolved peaks contribute to the area of the total response. For DROs, sum the area of all peaks eluting between C10 and C28. This area is generated by projecting a horizontal baseline between the retention times of C10 and C28. For DROs, a subtraction of the column bleed from the area of the DRO chromatogram is performed. A methylene chloride blank is analyzed during each 12-hour shift and the area is measured generated by projecting a horizontal baseline between the retention times for DROs and subtracted from the sample area.
For GROs, sum the area of all peaks eluting between 2-methylpentane and 1,2,4-trimethyl benzene.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass injected in nanograms
CF fuel= total peak area within retention time range/ analyte mass injected in nanograms

Concentration (µg/L) = Area analyte * Conc IS * Dilution factor * Vol of extract (µl)
/Area IS*mean CF (IC) *Vol sample extracted (ml) * 1000
Concentration (µg/Kg) = Area analyte * Conc IS * Dilution factor * Vol of extract injected (µl)
/Area IS*mean CF (IC) *weight sample (g) * 1000

VALIDATION ACTION:

9.1If the retention time criteria for both columns were not met, or if interference is present, all target compounds that are reported detected should be considered non-detected.
a. If the misidentified peak was sufficiently outside the retention time window, then the reported values may be a false positive and should be replaced with the sample CRQL value.
b. If the misidentified peak poses an interference with potential detection of a target peak, then the reported value should be considered and qualified as unusable (R).

9.2 If the data reviewer identifies a peak in both GC column analyses that falls within the appropriate retention time windows, but was reported as a non-detect, then the compound may be a false negative. Professional judgement should be used to decide if the compound should be included. All conclusions made regarding target compound identification should be included in the data review narrative.

9.3 If DROs or GROs exhibit marginal pattern-matching quality, professional judgement should be used to establish whether the differences are due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of a DRO or GRO is strongly suggested, results should be reported as presumptively present (N).

9.4 If GC or GC/MS confirmation was required but not performed, the reviewer should report this in the data validation report.

9.5 Quantitation limits affected by large, off-scale peaks should be qualified as unusable (R). If the interference is on-scale, the reviewer can provide an approximated quantitation limit (UJ) for each affected compound.

9.6 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other_____?
Actions: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement in quality data.

9.7 Were samples reanalyzed at the appropriate dilution when concentrations exceed linear range of the calibration curve?
Note: When sample dilution is performed, the laboratory typically reports two sets of sample data, diluted sample with responses within linear range and undiluted sample (least diluted sample is reported if two sets of dilutions were performed).
Action: Sample results quantitated with responses that exceed calibration range are approximated (J). In addition depending on data quality objectives of the project reanalysis of diluted extract may be required. Review resolutions in the narrative report.

9.8 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions and for soils, sample moisture?
Actions: If no and errors are large, request resubmittal of data package.

Document which sample analyses were reviewed and indicate frequency of raw data review, approximately 10% of data should be verified through raw data review. Show calculation below:

ADDITIONAL NOTES

O'Brien & Gere Engineers Data Validation Form
USEPA Method 8015B TPH- Nonhalogenated Organics/DRO/GRO
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Banks:_____
Project:_____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs:_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ PARTIAL VALIDATION
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington. D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8015B	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8015B	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses of TPH/DRO/GRO by USEPA SW-846 Method 8015B (GC/FID)

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*, Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Method 8015B. (National Functional Guidelines and Region V Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; for partial validation, raw data is not reviewed.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR TPH ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss issues with sample receipt or condition of samples.

1.2 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.3 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.4 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.5 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of results based on holding of the same from the time of sample collection to the time of preparation or analysis.

2.1 Method 8015B: Volatile samples must be analyzed within 14 days of collection. Semivolatile aqueous samples must be extracted within 7 days of collection and Soil/Sediment Samples must be extracted within 14 days from collection. Extracts must be analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Validation Actions:

a. If extraction holding times are exceeded associated sample results are flagged as estimated (UJ,J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than 2 times the criteria, nondetected sample results are rejected, (R), and detected sample results are approximated (J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries. Method 8015B did not recommend any surrogates to be used.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Validation Actions: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).
b. If %recovery is 10% to lower control limit, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, flag positive results as estimated (J).
d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.
e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.
f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
g. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.2 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action
Note: Surrogates -			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration for each group of samples of similar matrix and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards. If samples are expected to contain target compounds, the lab may use one MS and one unspiked duplicate sample. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

Validation Actions: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and detection limits (UJ).
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.3 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch for each sample matrix? Check the QAPP for frequency of LCS.

The LCS consists of clean matrix similar to the sample matrix and of the same weight or volume. The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards. If compliance monitoring, the spike concentration should be the regulatory limit or one to five times the background concentration (historical concentrations), whichever is greater. If no regulatory limits, the spike should be at 20 times the quantitation limit. Compare the recoveries to lab generated control limits.

Validation Actions: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).

b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).

c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).

d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. A method blank is analyzed to ensure that the GC system and solvents used are free of contamination.
Note for Region V, no "B" flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples of similar matrix extracted and analyzed?

Validation Actions: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results. Alternatively, field blank analyses can be used to evaluate overall contamination effects. However, method blanks are required for assessment of blank contamination for the instrument and solvents used by the lab.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.
6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

Actions levels are calculated at 5x blank value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.
Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected.

Validation Actions:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.4 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

7.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

7.2 Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

Section 7

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 6010B Metals, 7470A/7471A Mercury, 7951 Zinc (GTAA), 7211 Copper (GFAA), 9010B/9012A Cyanide – DRO/GRO – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 6010B Metals, 7470A/7471A Mercury, 7951 Zinc (GTAA), 7211 Copper (GFAA), 9010B/9012A Cyanide – DRO/GRO – Partial Validation

O'Brien & Gere Engineers Data Validation Form
USEPA Methods 6010B Metals, 7470A/7471A Mercury, 7951 Zinc (GFAA), 7211 Copper (GFAA), 9010B/9012A Cyanide
Date: _____ **Number of samples and compounds per sample:** _____
Project Number: _____
Validator: _____ **Equipment Banks:** _____
Project: _____ **Blind/Field Duplicates** _____
Laboratory: _____ **MS/MSDs** _____
QAPP: _____ **DV Guidelines: USEPA Region V**
Laboratory package number: _____ **FULL VALIDATION**
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Methods 3015/3051/6010B 7470A/7471A 9010B/9014 7951, 7211	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms

Analyses by USEPA Methods: 6010B Metals, 7470A/7471A Mercury, 7951 Zinc (GFAA), 7211 Copper (GFAA), 9010B/9012A Cyanide

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1993 *Standard Operating Procedure for Validation of CLP Inorganic Data*. Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*. EPA-540/R-94/013. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*. 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Methods 6010B, 7470A, 7471A, 7951, 7211, 9010B/9012A. (National Functional Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in thee sample.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross-checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR INORGANIC ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of inorganic data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, mg/L for waters and mg/kg dry weight for soils?

1.4 Were the raw data and digestion logs present for ICP/ flame AA and furnace AA, distillation logs for mercury and cyanide?

1.5 Were the raw data and digestion logs present for wet chemistry?

1.6 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.7 Were pH values for metals and mercury <2 and >12 for cyanide?
ACTION: If any sample was not preserved properly, all data should be flagged as estimated (UJ,J).

1.8 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample contains more than 90% water, all data should be qualified as unusable (R).

1.9 Were sample dilutions performed when necessary?

1.10 Were raw data to support analyses and QC operations present and complete?
ACTION: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in the non-compliance section of the final report.

1.11 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.12 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of results based on holding of the same from the time of sample collection to the time of preparation or analysis.

Holding time requirements from collection and preservation:

- Metal (6010B, 7951, 7211) analysis must be completed within 180 days; HNO3 to pH <2
- Mercury (7470A, 7471A) analysis must be completed within 28 days; HNO3 to pH <2
- Cyanide (9010B/9012A) analysis must be completed within 14 days; NaOH to pH >12, ascorbic acid in the presence of residual chlorine.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

2.1 Have any inorganic holding times, determined from date of collection to date of analysis, been exceeded?

2.2 Has the correct sample preservation been performed?

Validation Actions:

a. If holding times are not met for mercury or cyanide, qualify all results greater than the detection limit as estimated and results less than detection limit as estimated (UJ).
b. If holding times are exceeded for metals, reject detects and detection limits (R).
c. If holding times for mercury or cyanide are exceeded by two times the holding time criteria, reject detects and detection limits (R).

2.3 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab ID)	Analyte	Date Collected 1999	Date Analyzed 1999	Excursion (Number of days out) and Action

3.0 CALIBRATION

Method requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data for metals and inorganics. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run. Continuing calibration verification establishes that the initial calibration is still valid by checking the performance of the instrument on a continual basis.

Method notes:
Inductively coupled argon plasma atomic emission spectrometry (ICP-AES) allows simultaneous or rapid sequential determination of many elements in a short time. The disadvantage of ICP is background radiation from other elements and the plasma gases. ICP uses high-resolution optics and background correction to minimize these interferences. However, analysis for traces of inorganic analytes in the presence of large excess of a single analyte (high calcium) is difficult. ICP and direct aspiration or flame atomic absorption spectrometry (flame AA) have comparable detection limits. Flame AA analysis is relatively free of interelement spectral interferences. Graphite furnace atomic absorption spectrometry (GFAA) will exhibit lower detection limits than ICP or Flame AA, but the technique is so sensitive that interferences is a problem. Cold-vapor atomic absorption spectrometry (CVAA) uses a chemical reaction to reduce mercury selectively. The procedure is very sensitive, but is subject to interferences. Inductively coupled plasma mass spectrometry (ICP/MS) exhibits greater sensitivity than GFAA or flame AA, but isobaric elemental interferences, caused by different elements forming atomic ions with the same mass-to-charge ratio, is a problem. Mathematical corrections are used to minimize interferences in ICP/MS.

For ICP, acid digestion is required for all but prefiltered and acidified groundwater samples. Samples not digested must be matrix matched with standards. Detection limits, sensitivity, and linear concentrations ranges vary with the wavelength, spectrometer, matrix and operating conditions. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analytical line. In one mode of analysis the position used should be as free as possible from spectral interferences and should reflect the same change in background intensity as occurs at the analyte wavelength measured.

Interferences for ICP analysis:
Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of the high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.
Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternative wavelengths are desirable because of severe spectral interference.
Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by use of equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time at the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in the following table. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (false concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined in a sample containing 10 mg/L of Al. According to the table, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautions that other instruments may exhibit different levels of interference than shown on the table. The interference effect must be evaluated for each individual instrument, whether configured as sequential or simultaneous instrument. When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interferences that may be specific the instrument or the matrix. Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest. Samples that show an elevated background emission may be background corrected by applying a correction factor.

If the correction routine is operating properly, the determined apparent analyte concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank (multiplying concentration of the interfering element by the value of the correction factor/10). If after the subtraction of the calibration blank the analyte concentration falls outside of this range, a change in the correction factor of more than 10% should be suspected.

When interelement corrections are applied, spectral interference check solutions are analyzed daily for verification. If the correction factors are found to be within the 20% criteria for 5 consecutive days, the frequency is extended to weekly. If the nature of the samples is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement correction factors must be verified and updated every 6 months or when an instrument change occurs.

When interelement corrections are not used the following may be applied: a computer software routine to notify the analyst when an interfering element is detected, or analysis of the interference check sample which contains similar concentrations of the major components of the samples on a continuing basis to verify the absence of effects at the wavelengths selected.

Physical interferences, associated with sample nebulization and transport, are reduced by diluting the sample, using a peristaltic pump, using an internal standard, or by using a high solids nebulizer.

Chemical interferences include molecular compound formation, ionization effects, and vaporization effects. These are controlled by selection of operating conditions, buffering of samples, matrix matching, and standard additions.

Memory interferences, resulting when analytes in a previous sample contribute to the signals in the next sample, are controlled by adjusting the rinse periods and the use of rinse blanks.

Potential Interferences for ICP
Analyte Concentration Equivalents Arising From Interference at the 100 mg/L Level

Analyte	Wavelength (nm)	Interferant									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Al	308.215	-	-	-	-	-	-	0.21	-	-	1.4
Sb	206.833	0.47	-	2.9	-	0.08	-	-	-	0.25	0.45
As	193.696	1.3	-	0.44	-	-	-	-	-	-	1.1
Ba	455.403	-	-	-	-	-	-	-	-	-	-
Be	313.042	-	-	-	-	-	-	-	-	0.04	0.05
Cd	226.502	-	-	-	-	0.03	-	-	0.02	-	-
Ca	317.933	-	-	0.08	-	0.01	0.01	0.04	-	0.03	0.03
Cr	267.716	-	-	-	-	0.003	-	0.04	-	-	0.04
Co	228.616	-	-	0.03	-	0.005	-	-	0.03	0.15	-
Cu	324.754	-	-	-	-	0.003	-	-	-	0.05	0.02
Fe	259.940	-	-	-	-	-	-	0.12	-	-	-
Pb	220.353	0.17	-	-	-	-	-	-	-	-	-
Mg	279.079	-	0.02	0.11	-	0.13	-	0.25	-	0.07	0.12
Mn	257.610	0.005	-	0.01	-	0.002	0.002	-	-	-	-
Mo	202.030	0.05	-	-	-	0.03	-	-	-	-	-
Ni	231.604	-	-	-	-	-	-	-	-	-	-
Se	196.026	0.23	-	-	-	0.09	-	-	-	-	-
Na	588.995	-	-	-	-	-	-	-	-	0.08	-
Tl	190.864	0.30	-	-	-	-	-	-	-	-	-
V	292.402	-	-	0.05	-	0.005	-	-	-	0.02	-
Zn	213.856	-	-	-	0.14	-	-	-	0.29	-	-

Note:
Dashes indicate that interference was not observed, even with interferents at elevated concentrations.
The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.
Interferences will be affected by background choice; other intereferences may be present.

For ICP:
Mixed calibration standards, prepared using the same types and volumes as the samples. Each standard mixture should be analyzed separately to determine possible spectral interferences or impurities. The calibration curve consists of a blank and a standard.
Calibration blanks are prepared using the same concentrations of the acids in the standards and the samples. The blanks are used to flush the system between standards and before samples and for all initial and continuing calibration blank determinations. A calibration blank is analyzed immediately after the ICV and CCV. The results are to be within three times the IDL. If the blank is less than $1/10^{th}$ the concentration of the action limit and no sample is within of the action limit, corrections are not performed.
Method blanks must contain all the reagents in the same volumes as used in the sample processing and must be carried through the complete preparation procedure as the samples. One method blank is prepared for each batch of samples.
The initial calibration verification (ICV) is prepared from a standard source different from the calibration standard at a concentration within the calibration range. Check the calibration with the ICV following the initial calibration.
The continuing calibration verification (CCV) is prepared in the same acid matrix, using the same standards as the calibration at a concentration near the mid-point of the calibration curve. The CCV is analyzed immediately following daily calibration, and after every tenth sample and at the end of the analytical sequence.
The ICV and CCV must be within 10% of the calibration with a relative standard deviation of < 5% from replicate integrations. Otherwise, the sample analysis is discontinued, the cause determined, the instrument is recalibrated, and all samples following the last acceptable ICV or CCV must be reanalyzed..

Although not required, the calibration near the detection limit (CRI) may be analyzed at the beginning and end of the analytical sequence, or at a minimum of twice per 8-hour working shift. The CRI is two times the contract required detection limit (CRDL) or two times the instrument detection limit, whichever is greater for all analytes except Al, Ba, Ca, Fe, Mg, Na, and K. Laboratory limits are used to evaluate the recovery of the CRI.

The interference check solution contains known concentrations of interfering elements to test the correction factors. The elements of interest are spiked at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, the spiking will not be necessary. The check solution must agree within 20% of the expected value. Otherwise, the problem is corrected and the instrument recalibrated.
An initial demonstration of performance for background correction points, upper limits of the dynamic range, method and instrument detection limits, determination and verification of interelement correction equations, using the same instrument, operating conditions, and calibration routine as the samples. The optimized operating conditions should provide the lowest reliable instrument detection limits and method detection limits. The upper dynamic range should be checked every 6 months.

The method of standard additions (MSA) is used if interference is suspected or if a new matrix is analyzed. The standards are added at one or more levels to aliquots of the sample. The MSA compensates for enhancement or depression of an analyte signal by a matrix. The single method consists of adding standard to the first aliquot of sample, and adding acid blank at the same volume as the standard to the second aliquot.

The calculation:
Concentration = Intensity unfortified * volume of standard * concentration of standard
/ intensity fortified – intensity unfortified * volume sample
A second option is to use several fortified portions and linear regression analysis.
Samples with concentrations that exceed the linear calibration range are diluted and reanalyzed.
All results should be reported with up to three significant figures.

For mercury analysis: The CVAA is used; the mercury is reduced to the elemental state and aerated from solution in a closed system. The absorbance of the mercury vapor is measured as a function of concentration. A final volume of 100 milliliters (using BOD bottles) is used for analysis.
Five standards and one blank are prepared each day of analysis for the calibration curve. The absorption versus micrograms of mercury is plotted. The mercury concentration is read from the calibration curve, or MSA is used. After calibration, the curve is verified by a calibration blank and a calibration check standard made from a source independent from the calibration standard at mid-range is used. The ICV must be within 10% of the true value to verify the curve. The CCV is analyzed after every 10 samples; this must be within 20% of the true value or the previous samples must be reanalyzed. If the sample matrix is so complex that viscosity, surface tension, and components can't be accurately matched with standards, MSA is used.

Although not required, the calibration near the detection limit (CRA) may be analyzed at the beginning of the analytical sequence after the ICV. The CRA is at the contract required detection limit (CRDL) or the instrument detection limit, whichever is greater. Laboratory limits are used to evaluate the recovery of the CRA.

For GFAA analysis:

A minimum of three standards and one blank are prepared each day of analysis for the calibration curve. Background correction must be performed; otherwise sample absorbance will be greater than it should be and the result will be erroneously high. After calibration, the curve is verified by a calibration blank and a calibration check standard made from a source independent from the calibration standard at mid-range is used. The ICV must be within 10% of the true value to verify the curve. The CCV is analyzed after every 10 samples; this must be within 20% of the true value or the previous samples must be reanalyzed. If the sample matrix is so complex that viscosity, surface tension, and components can't be accurately matched with standards, MSA is used. If the sample concentration is greater than the upper range of the calibration curve, samples are diluted in the same acid matrix and reanalyzed.

Although not required, the calibration near the detection limit (CRA) may be analyzed at the beginning of the analytical sequence after the ICV. The CRA is prepared at the contract required detection limit (CRDL) or the instrument detection limit, whichever is greater. Laboratory limits are used to evaluate the recovery of the CRA.

For cyanide analysis; A reflux-distillation procedure using a strong acid and magnesium catalyst, is used to extract cyanide salts and insoluble cyanide. Both total and cyanide amenable to chlorination are determined by this technique. Reactive cyanide, generated by exposure to mild acid, is not determined by this method. Cyanide in the form of hydrocyanic acid (HCN) is purged from the sample and captured into a alkaline scrubber solution. The concentration of cyanide in the scrubber is then determined. Oxidizing such as chlorine decomposes most cyanides. After determining that chlorine is present, sodium arsenite solution or ascorbic acid is added to samples to remove the chlorine. Sulfide interference is removed by adding bismuth nitrate to waste before distillation. Interference of nitrate/nitrite is removed by pretreatment with sulfamic acid before distillation. Aqueous samples are preserved by adding 50% NaOH until the pH is greater than or equal to 12 at the time of collection. The final volume of the scrubber is 250 milliliters. Six calibration standards for samples without sulfide range from 20 to 400 µg/L. The absorbance of the standards versus the cyanide concentration is used to quantitate the sample results. For samples with sulfide, five standards ranging from 20 to 400 µg/L are prepared in the same manner as the samples. Two standards (high and low) should be distilled and compared to similar values on the calibration curve to check the distillation procedure. The values should compare within 10% of the undistilled standards. The calibration curve is verified for every sample batch by the analysis of a calibration standard that is prepared from independent sources. The standard must be within 15%of the expected value. The method of standard additions is used for analysis of samples that have matrix interferences, such as samples that contain sulfides.

Correlation coefficients for calibration curves should be ≥ 0.995 to ensure linearity over the calibration range.

Check for transcription/calculation calibration errors. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory.

3.1 Did the laboratory use the proper number of standards for calibration, at the proper concentration and was the calibration frequency performed as required?

ACTION: Qualify associated detected sample results as approximate (J) and reject detection limits (R)

ICP

GFAA

CN

Hg

3.2 Did the laboratory prepare and analyze CRI or CRA standards?

Note if recoveries were within laboratory criteria. Otherwise use 75-125% as control limits.

Action: Qualify associated detected sample results as approximate (J) and detection limits as estimated (UJ).

3.3 Were the correlation coefficients for the calibration curves for mercury, cyanide and GFAA methods $\geq$ 0.995? Note if the calibration curve was generated using a computer assisted second degree fit. If not, qualify as follows.
Action: Qualify associated detected sample results as approximate (J) and detection limits as estimated (UJ).

GFAA

Hg

CN

3.4 Was one of the midrange cyanide standards distilled and within 10% of the undistilled standards?
Action: Qualify associated detected sample results as approximate (J) and detection limits as estimated (UJ).

3.5 Were initial and continuing calibration verification standards (ICV, CCV) within criteria?
ICP/GFAA – 90-110%
Mercury – 80-120%
Cyanide – 85-115%

Action:

ICP/GFAA:	Recoveries between 75-89%, or 111%-125%: (J) for positive results. Recoveries 111-125%: detection limits are acceptable. Recoveries 75-89%: (UJ) for nondetected results. Recoveries <75%: reject positive results (R). Recoveries >125%: positive results are rejected (R) and nondetected results are acceptable.
Mercury	Recoveries between 65-79%, or 121%-135%: (J) for positive results. Recoveries 121-135%: detection limits are acceptable. Recoveries 65-79%: (UJ) for nondetected results. Recoveries <65%: reject positive results (R). Recoveries >135%: positive results are rejected (R) and nondetected results are acceptable.
Cyanide	Recoveries between 70-84%, or 116%-130%: (J) for positive results. Recoveries 116-130%: detection limits are acceptable. Recoveries 70-84%: (UJ) for nondetected results. Recoveries <70%: reject positive results (R). Recoveries >130%: positive results are rejected (R) and nondetected results are acceptable.

3.6 Was adequate calibration information provided?
Action: If no immediately contact laboratory for additional information and explanation. If calibration data cannot be provided, immediately contact Project Manager.
Verify calibrations by review of raw data. Check ICV/CCV calculation for each type of analysis performed.

3.7 List below initial and calibration verifications and samples qualified due to calibration excursions.

Unique ICV/CCV Identification	Analyte	%Recovery	Action	Samples Affected (client/lab ID)

4.0 BLANK ANALYSIS

The assessment of blank analysis results is to determine the existence and magnitude of contamination resulting from laboratory or field activities. The criteria for evaluation of blanks applies to any blank associated with the samples (method, calibration, field). If problems with any blank exist, all associated data must be evaluated to determine whether or not there is a variability in the data or if the problem is an isolated occurrence. The blanks include preparation/method blank, calibration blanks, and field blanks.

The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations.
The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.
Use a calibration blank immediately following daily calibration, after every 10 samples and at the end of the analytical run.
Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample.
The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

The blank analyses may not involve the same weights, volumes, or dilutions as the associated samples. It may be easier to work from the raw data to compare blank and sample concentrations.

4.1 Were the initial calibration blanks (ICBs) analyzed after ICVs?

4.2 Were continuing calibration blanks (CCBs) analyzed after every CCV?

4.3 Was one preparation/method blank prepared for each matrix and with each batch of samples digested?

Action: If no for the above, qualify the positive sample results and detection limits as approximate (UJ,J).

4.4 Was a field blank analyzed in accordance with the QAPP?

Data is qualified using the highest concentration detected in the associated blank samples. The blanks include preparation/method blank, calibration blanks, and field blanks.

4.5 Apply the following to samples:

a- For blanks with analytes greater than the IDL but less than five times the reported detection, associated sample results less than five times the blank concentration are qualified as undetected (U) and sample results greater than five times the blank concentration are qualified as approximate (J).

b- Sample concentrations associated with a blank with a negative result whose absolute value is greater than the reported detection limit is rejected (R).

c- For blanks with analytes greater than five times the reported detection limit, all associated samples are rejected

(R) since the system is considered to be out of control.

4.6 Summarize the samples qualified due to blank excursions.

Unique Blank ID	Analyte	Concentration	Action Level	Samples Affected (client/lab) ID

5.0 ICP INTERFERENCE CHECK SAMPLE ANALYSIS

The ICP interference check sample verifies interelement and background correction factors. Solution A which contains the interferents (Al, Ca, or Mg typically at 500 mg/L , Fe at 200 mg/L), and solution AB which contains the analytes (at 0.5, 1.0 mg/L) mixed with the interferents are analyzed. Both solutions are analyzed for all wavelengths used for each analyte reported by ICP at the beginning of each analytical run. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, the spiking will not be necessary. The check solution must agree within 20% of the expected value. Otherwise, the problem is corrected and the instrument recalibrated.

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.1 Were ICP ICS analyses performed at the required frequency?
Action: Qualify the associated sample results as approximate (UJ,J).

5.2 Were the recoveries for ICS AB within 80-120% recovery and ICSA concentrations < instrument reporting limits?
Recalculate from the raw data one or more of the analyte percent recoveries (%R) using the following equation, and verify that the recalculated value agrees with the laboratory reported values.
ICS %R = Found Solution AB /True Solution AB *100
Where:
Found Solution AB = concentration (in µg/L) of each analyte measured in the analysis of solution AB.
True Solution AB = concentration (in µg/L) of each analyte in solution AB.

ACTION: Qualification is only necessary for those samples in which the concentrations of interferents (Aluminum, calcium, iron, and magnesium) are comparable to or greater than the levels of the corresponding ICS solution.

a. If %recovery is > 120% and the sample results are < IDL, no action is taken.
b. If % recovery is >120% and the sample results are > IDL, qualify associated sample results as approximate (J).
c. If % recovery is 50-79% and the sample results are > IDL, qualify associated sample results as approximate (J).
d. If sample results are < IDL and the % recovery is 50-79%, qualify associated sample results as estimated (UJ) due to the possibility of false negatives.
e. If % recovery is < 50%, qualify associated sample results as rejected (R).
f. If results > 2 times the IDL are observed for elements which are not present in the ICSA solution, associated sample results with analyte concentrations that are comparable to those levels found in the ICS (false positive) are qualified as approximate (J).
g. If negative results are observed for elements that are not present in the ICS solution and their absolute value is > IDL, associated sample results with analyte concentrations < IDL are qualified as approximate (UJ).

5.3 Summarize below ICP ICS analyses and samples qualified due to ICP ICS excursions.

Unique ICS ID	Analyte	%Recovery	Action	Samples Affected (client/lab)

6.0 MATRIX SPIKE ANALYSIS

The matrix spike is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. If the spike is added to the sample prior to distillation or digestion, it is a predigestion/predistillation or matrix spike. If the spike is added to after the completion of the distillation or digestion it is a post-digestion/post-distillation spike. Matrix spike recoveries are evaluated based on method or laboratory generated control limits.

6.1 Were field blanks used for the matrix spike?
6.2 Was one matrix spike prepared and analyzed for each group of samples with similar matrix for each delivery group?
6.3 If the pre-digestion/pre-distillation spike exceeded control limits, was a post-digestion spike performed?
Action: If no for the previous questions, qualify the associated sample results as approximate (UJ,J). Post-digestion spikes are evaluated using the same criteria as matrix spikes.

6.4 Was the recovery within control limits? ? A control limit of 75-125% applies to metals, otherwise laboratory control limits are used.
6.5 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

The spike recovery limits do not apply when the sample concentration exceeds the spike concentration by a factor of 4 or greater. If more than one spiked sample result per matrix and for each group of samples, and one spiked recovery is not within criteria, qualify all of the samples in the same matrix and group.

ACTION:

Recoveries less than 30%: detection limits are rejected (R)
Recoveries between lower control limit and 30%: detection limits are qualified as approximate (UJ)
Recoveries greater than upper control limit or less than lower control limit: positive sample results are qualified as approximate (J)
Recoveries greater than upper control limit: detection limits are acceptable.

6.6 Summarize below MS/MSD analyses and samples qualified due to MS/MSD excursions.
Note: If sample concentration exceeds the spike concentration by a factor of 4 or more, no action is taken.
Note: If more than one spike is analyzed and one is not within criteria, flag all samples.

Unique MS ID	Analyte	%Recovery bias [control limits]	Action	Samples Affected (client/lab ID)

7.0 LABORATORY DUPLICATE AND MSD ANALYSIS

Duplicate sample determinations are used to demonstrate acceptable method precision by the laboratory at the time of analysis. Precision is than evaluated by calculating RPD between the two results.

7.1 Were field blanks used for the laboratory duplicate?
7.2 Was one laboratory duplicate prepared and analyzed for each group of samples with similar matrix for each delivery group?

Action: If no for the previous questions, qualify the associated sample results as approximate (UJ,J). Post-digestion spikes are not used to qualify sample results.

7.3 Was the RPD within control limits? For laboratory duplicates; a control limit of 20% applies to metals, otherwise laboratory control limits are used.
7.4 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

Check the raw data and recalculate one or more of the RPD values using the following equation to verify that the results have been correctly reported.

RPD = |S-D| / (S+D)/2 *100

Where:

RPD = Relative Percent Difference
S = First Sample Value (original sample)
D = Second Sample Value (duplicate)

If any result is less than 5 times the reporting limit, a control limit of ± the reporting limit is used to evaluate the result.

ACTION: Qualify associated sample results of the same matrix as approximate (UJ,J).

7.5 List below laboratory duplicates /MSD samples and samples qualified due to duplicate excursions.

Unique Duplicate ID	Analyte	Excursion [control limit]	Action	Samples Affected (client/lab ID)

8.0 LABORATORY CONTROL SAMPLE (LCS)

The laboratory control sample serves as a monitor of the performance of each step during the analysis, including the sample preparation. If criteria are not met, the laboratory performance and method accuracy are in question. Laboratory control limits are used to evaluated the LCS recoveries.

8.1 Were LCSs analyzed for each sample matrix, for each digestion/distillation batch?
Action: If no, note in the data validation report. Flag as approximate associated results (UJ,J) for those analytes in which LCS was not analyzed.
8.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

8.3 Were the control limits met?
Action for aqueous samples:

For recoveries less than lower control limits but greater than 50% or greater than upper limits: positive sample results are qualified as approximate (J)
For recoveries greater than the upper control limit: detection limits are acceptable
For recoveries greater than 50% but less than the lower control limit: detection limits are qualified as approximate (UJ)
For recoveries less than 50%: sample results are rejected (R)

Action for soil samples:

For recoveries less than lower control limits or greater than upper limits: positive sample results are qualified as approximate (J)
For recoveries greater than the upper control limit: detection limits are acceptable
For recoveries less than lower control limit: detection limits are qualified as approximate (UJ)

8.4 List LCS analyses and samples qualified due to LCS excursions.

Unique LCS ID	Analyte	%Recovery bias [control limit]	Action	Samples Affected (client/lab ID)

9.0 SERIAL DILUTION ANALYSIS

Although not required by method 6010B, the serial dilution analysis (five-fold dilution) is performed to evaluate whether significant chemical and physical interferences are present due to sample matrix. The serial dilution analysis must agree within a 10% difference of the original determination after correction for dilution.
Note: Serial dilutions are only required for initial concentrations ≥50 times the IDL for ICP analysis.

Dilution test - For GFAA, for each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis described below. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions.

9.1 Was a serial dilution performed for each sample matrix for each group of samples as required?
Action: If no, note in the data validation report.

9.2 Was field blank used?
Action: Note in the data validation report.

9.3 Are results outside of control limits; was a positive or negative interference exhibited?
Action: Qualify associated sample results in the same group and matrix as approximate (UJ,J) regardless of whether a positive or negative interference was exhibited.

Check the raw data and recalculate the %D using the following equation.
$\%D = |I-S| / I \times 100$
Where:
I = Initial Sample Result
S = Serial Dilution Result (Instrument Reading x 5)

If evidence of negative interference is found, professional judgement must be used to qualify the associated sample data. The potential effects on the reported data should be noted in the data validation report.

If more than one serial dilution is performed and exceeds criteria, all associated sample results are qualified.

9.4 List serial dilution analyses and samples qualified due to serial dilution excursions.

Unique Serial Dilution ID	Analyte	%Difference	Action	Samples Affected (client/lab ID)

10.0 VERIFICATION OF INSTRUMENT PARAMETERS AND RESULTS

10.1 Are the following present for metals:

- instrument detection limits
- ICP linear ranges
- ICP interelement correction factors

Action: Document in the data validation report.

10.2 Were the instrument detection limits present for the remaining inorganic analytes?
Action: Document in the data validation report.

11.0 FIELD DUPLICATE

Field duplicates, which are blind field samples submitted to the laboratory for analysis, demonstrate sample collection precision. Precision is than evaluated by calculating RPD between the two results.

11.1 Was a field duplicate collected and analyzed according to the QAPP?

Action: If no for the previous question, note in the data validation report that field precision was not evaluated.

11.2 Was the RPD within control limits? For field duplicates consult the QAPP. For field duplicates; a control limit of 20% applies to metals, otherwise laboratory control limits are used. If any result is less than 5 times the reporting limit, a control limit of ± the reporting limit is used to evaluate the result.

Action: Qualify associated sample results of the same matrix as approximate (UJ,J).

11.2 Summarize below samples qualified due to field duplicate excursions.

Field Duplicate ID	Analyte	Excursion	Actions	Samples Affected (client/lab ID)

12.0 GRAPHITE FURNACE ATOMIC ABSORPTION ANALYSIS

Because of the nature of the GFAA analysis, special analytical techniques are required. Although not required by the method, duplicate injections and multiple level furnace post digestion spikes may be used to establish precision and accuracy of the individual analytical determinations. If the post-digestion spike recovery exceeds criteria, the method of standard additions is performed.

12.1 Were duplicate injections performed for each sample?.

12.2 Do the duplicate injections agree within 20% RSD?
If no, was the sample reanalyzed?

12.3 Is the analytical spike recovery within the control limits of 85-115%?

Check the raw data for duplicate injection and analytical spike results.

Action:
If duplicate injection/spike was performed and failed criteria, qualify sample results as approximate (UJ,J)
Flag data only when samples were not subsequently analyzed by MSA.

12.4 List samples qualified due to graphite furnace atomic absorption excursions.

Sample ID (client/lab ID)	Analyte	Excursion	Action

13.0 METHODS OF STANDARD ADDITIONS (MSA) ANALYSIS

The MSA should be used if an interference is suspected or a new matrix is encountered for inorganic analyses. When the MSA is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. The simplest version is the single addition method. To the first aliquot (A), a known volume of standard is added and to the second aliquot (B), the same volume of solvent is added. The concentration is calculated by:
Concentration = Signal B * Volume Solvent * Concentration of standard/ Signal A – Signal B * Volume added

For more than one fortified portion of the prepared sample, linear regression analysis can be applied to obtain the concentration of the sample solution. A series of standard additions are prepared; One should be prepared so that the resulting concentration is 50% of the expected absorbance from the analyte, the second and third should be prepared so that the concentrations are 100% and 150% of the expected sample absorbance. The absorbance is plotted versus the concentrations and the resulting line is extrapolated to zero absorbance. The point of the interception is the concentration of the analyte in the sample. The curve of the MSA must be linear over the range of interest; the correlation coefficient must be ≥ 0.995.

For AA methods, if the serial dilution result exceeds criterion, a post-digestion spike is performed. If the results of the post-digestion spike exceed criteria (85-115%) the MSA is performed.

For GFAA:
Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.
The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V , are taken. To the first (labeled A) is added a known volume V x S of a standard analyte solution of concentration C . To the second aliquot S (labeled B) is added the same volume V of the solvent. The analytical S signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C is calculated. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.
Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.
For the results of this MSA technique to be valid, the following limitations must be taken into consideration:
1. The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.
2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.
3. The determination must be free of spectral interference and corrected for nonspecific background interference.

For cyanide, MSA should be used for samples that exhibit matrix interference.

13.1 Was MSA performed when required using the appropriate technique ?
Action: Qualify sample results as approximate (UJ,J).

13.2 Is the correlation coefficient for MSA less than 0.995?
Action: Qualify sample results as approximate (UJ,J).

13.3 List below samples qualified due to MSA excursions.

Sample ID (client/lab)	Analyte	Excursion	Action

14.0 ANALYTE QUANTITATION AND REPORTED DETECTION LIMITS

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

The objective is to ensure that the reported sample quantitation results are accurate.

14.1 Were sample weights, volumes and dilutions taken into account when reporting sample results and detection limits?

Actions: If no sample results may be inaccurate; note necessary changes and request resubmittals of laboratory packages.

14.2 Were samples reanalyzed at the appropriate dilution, when concentrations exceed linear range of the calibration curve?

Action: Qualify sample results as approximate (J).

The raw data should be examined to verify that the correct calculation of the sample results was reported by the laboratory. Digestion and distillation logs, instrument printouts, strip charts, etc. should be compared to the reported sample results recorded on the Inorganic Forms.

Examine the raw data for any anomalies (i.e., baseline shifts, negative absorbance, omissions, legibility, etc.).

Sample calculation:

Concentration (µg/L) = Concentration from curve (µg/L) * Dilution factor

Concentration (µg/Kg) = Concentration from curve (µg/L) * Final volume (ml) * Dilution factor / Weight of sample

Document which sample analyses were reviewed and indicate frequency of raw data review, approximately 10% of data should be verified through raw data review. Show calculation below:

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form
USEPA Methods 6010B Metals, 7470A/7471A Mercury, 7951 Zinc (GFAA), 7211 Copper (GFAA), 9010B/9012A Cyanide
Date:_____ Number of samples and compounds per sample:_____
Project Number:_____
Validator:_____ Equipment Banks:_____
Project:_____ Blind/Field Duplicates:_____
Laboratory:_____ MS/MSDs_____
QAPP:_____ DV Guidelines: USEPA Region V
Laboratory package number:_____ PARTIAL VALIDATION
Method reference:
USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846).* 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Methods 3015/3051/6010B 7470A/7471A 9010B/9014 7951, 7211	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Methods 3015/3051/6010B 7470A/7471A 9010B/9014 7951, 7211	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms

Analyses by USEPA Methods: 6010B Metals, 7470A/7471A Mercury, 7951 Zinc (GFAA), 7211 Copper (GFAA), 9010B/9012A Cyanide

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1993 *Standard Operating Procedure for Validation of CLP Inorganic Data.* Chicago, Illinois and
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review.* EPA-540/R-94/013. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846),* 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA SW-846 Methods 6010B, 7470A, 7471A, 7951, 7211, 9010B/9012A. (National Functional Guidelines apply to USEPA CLP Methods rather than SW-846 Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in thee sample.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; for partial validation, raw data is not reviewed.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR INORGANIC ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues with sample receipt or condition of samples.

1.2 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.3 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample contains more than 90% water, all data should be qualified as unusable (R).

1.4 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.5 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of results based on holding of the same from the time of sample collection to the time of preparation or analysis.

Holding time requirements from collection and preservation:

- Metal (6010B, 7951, 7211) analysis must be completed within 180 days; HNO3 to pH <2
- Mercury (7470A, 7471A) analysis must be completed within 28 days; HNO3 to pH <2
- Cyanide (9010B/9012A) analysis must be completed within 14 days; NaOH to pH >12, ascorbic acid in the presence of residual chlorine.

2.1 Have any inorganic holding times, determined from date of collection to date of analysis, been exceeded?

2.2 Has the correct sample preservation been performed?

Validation Actions:

a. If holding times are not met for mercury or cyanide, qualify all results greater than the detection limit as estimated and results less than detection limit as estimated (UJ).
b. If holding times are exceeded for metals, reject detects and detection limits (R).
c. If holding times for mercury or cyanide are exceeded by two times the holding time criteria, reject detects and detection limits (R).

2.3 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab ID)	Analyte	Date Collected 1999	Date Analyzed 1999	Excursion (Number of days out) and Action

3.0 Blank Analysis

The assessment of blank analysis results is to determine the existence and magnitude of contamination resulting from laboratory or field activities. The criteria for evaluation of blanks applies to any blank associated with the samples (method, calibration, field). If problems with any blank exist, all associated data must be evaluated to determine whether or not there is a variability in the data or if the problem is an isolated occurrence. The blanks include preparation/method blank, calibration blanks, and field blanks.

The blank analyses may not involve the same weights, volumes, or dilutions as the associated samples. It may be easier to work from the raw data to compare blank and sample concentrations.

3.1 Was one preparation/method blank prepared for each matrix and with each batch of samples digested?

Action: If no for the above, qualify the positive sample results and detection limits as approximate (UJ,J).

3.2 Was a field blank analyzed in accordance with the QAPP?

Data is qualified using the highest concentration detected in the associated blank samples. The blanks include preparation/method blank, calibration blanks, and field blanks.

3.3 Apply the following to samples:

a- For blanks with analytes greater than the IDL but less than five times the reported detection, associated sample results less than five times the blank concentration are qualified as undetected (U) and sample results greater than five times the blank concentration are qualified as approximate (J).

b- Sample concentrations associated with a blank with a negative result whose absolute value is greater than the reported detection limit is rejected (R).

c- For blanks with analytes greater than five times the reported detection limit, all associated samples are rejected (R) since the system is considered to be out of control.

3.4 Summarize the samples qualified due to blank excursions.

Unique Blank ID	Analyte	Concentration	Action Level	Samples Affected (client/lab) ID

4.0 ICP INTERFERENCE CHECK SAMPLE ANALYSIS

The ICP interference check sample verifies interelement and background correction factors. Solution A which contains the interferents (Al, Ca, or Mg typically at 500 mg/L , Fe at 200 mg/L), and solution AB which contains the analytes (at 0.5, 1.0 mg/L) mixed with the interferents are analyzed. Both solutions are analyzed for all wavelengths used for each analyte reported by ICP at the beginning of each analytical run. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, the spiking will not be necessary. The check solution must agree within 20% of the expected value. Otherwise, the problem is corrected and the instrument recalibrated.

4.1 Were the recoveries for ICS AB within 80-120% recovery and ICSA concentrations < instrument reporting limits?

Action: Qualification is only necessary for those samples in which the concentrations of interferents (Aluminum, calcium, iron, and magnesium) are comparable to or greater than the levels of the corresponding ICS solution.

a. If %recovery is > 120% and the sample results are < IDL, no action is taken.
b. If % recovery is >120% and the sample results are > IDL, qualify associated sample results as approximate (J).
c. If % recovery is 50-79% and the sample results are > IDL, qualify associated sample results as approximate (J).
d. If sample results are < IDL and the % recovery is 50-79%, qualify associated sample results as estimated (UJ) due to the possibility of false negatives.
e. If % recovery is < 50%, qualify associated sample results as rejected (R).
f. If results > 2 times the IDL are observed for elements which are not present in the ICSA solution, associated sample results with analyte concentrations that are comparable to those levels found in the ICS (false positive) are qualified as approximate (J).
g. If negative results are observed for elements that are not present in the ICS solution and their absolute value is > IDL, associated sample results with analyte concentrations < IDL are qualified as approximate (UJ).

4.2 Summarize below ICP ICS analyses and samples qualified due to ICP ICS excursions.

Unique ICS ID	Analyte	%Recovery	Action	Samples Affected (client/lab)

5.0 MATRIX SPIKE ANALYSIS

The matrix spike is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. If the spike is added to the sample prior to distillation or digestion, it is a predigestion/predistillation or matrix spike. If the spike is added to after the completion of the distillation or digestion it is a post-digestion/post-distillation spike. Matrix spike recoveries are evaluated based on method or laboratory generated control limits.

5.1 Were field blanks used for the matrix spike?

5.2 Was one matrix spike prepared and analyzed for each group of samples with similar matrix for each delivery group?

ACTION: If no for the previous questions, qualify the associated sample results as approximate (UJ,J). Post-digestion spikes are evaluated using the same criteria as matrix spikes.

5.3 Was the recovery within control limits? ? A control limit of 75-125% applies to metals, otherwise laboratory control limits are used.

The spike recovery limits do not apply when the sample concentration exceeds the spike concentration by a factor of 4 or greater. If more than one spiked sample result per matrix and for each group of samples, and one spiked recovery is not within criteria, qualify all of the samples in the same matrix and group.

ACTION:

Recoveries less than 30%: detection limits are rejected (R)
Recoveries between lower control limit and 30%: detection limits are qualified as approximate (UJ)
Recoveries greater than upper control limit or less than lower control limit: positive sample results are qualified as approximate (J)
Recoveries greater than upper control limit: detection limits are acceptable.

5.4 Summarize below MS/MSD analyses and samples qualified due to MS/MSD excursions.
Note: If sample concentration exceeds the spike concentration by a factor of 4 or more, no action is taken.
Note: If more than one spike is analyzed and one is not within criteria, flag all samples.

Unique MS ID	Analyte	%Recovery bias [control limits]	Action	Samples Affected (client/lab ID)

6.0 LABORATORY DUPLICATE AND MSD ANALYSIS

Duplicate sample determinations are used to demonstrate acceptable method precision by the laboratory at the time of analysis. Precision is than evaluated by calculating RPD between the two results.

6.1 Were field blanks used for the laboratory duplicate?
6.2 Was one laboratory duplicate prepared and analyzed for each group of samples with similar matrix for each delivery group?
Action: If no for the previous questions, qualify the associated sample results as approximate (UJ,J). Post-digestion spikes are not used to qualify sample results.

6.3 Was the RPD within control limits? For laboratory duplicates; a control limit of 20% applies to metals, otherwise laboratory control limits are used.

If any result is less than 5 times the reporting limit, a control limit of ± the reporting limit is used to evaluate the result.

Action: Qualify associated sample results of the same matrix as approximate (UJ,J).

6.4 List below laboratory duplicates /MSD samples and samples qualified due to duplicate excursions.

Unique Duplicate ID	Analyte	Excursion [control limit]	Action	Samples Affected (client/lab ID)

7.0 LABORATORY CONTROL SAMPLE (LCS)

The laboratory control sample serves as a monitor of the performance of each step during the analysis, including the sample preparation. If criteria are not met, the laboratory performance and method accuracy are in question. Laboratory control limits are used to evaluated the LCS recoveries.

7.1 Were LCSs analyzed for each sample matrix, for each digestion/distillation batch?
Action: If no, note in the data validation report. Flag as approximate associated results (UJ,J) for those analytes in which LCS was not analyzed.

7.2 Were the control limits met?
Action for aqueous samples:

For recoveries less than lower control limits but greater than 50% or greater than upper limits: positive sample results are qualified as approximate (J)
For recoveries greater than the upper control limit: detection limits are acceptable
For recoveries greater than 50% but less than the lower control limit: detection limits are qualified as approximate (UJ)
For recoveries less than 50%: sample results are rejected (R)

Action for soil samples:

For recoveries less than lower control limits or greater than upper limits: positive sample results are qualified as approximate (J)
For recoveries greater than the upper control limit: detection limits are acceptable
For recoveries less than lower control limit: detection limits are qualified as approximate (UJ)

7.3 List LCS analyses and samples qualified due to LCS excursions.

Unique LCS ID	Analyte	%Recovery bias [control limit]	Action	Samples Affected (client/lab ID)

8.0 SERIAL DILUTION ANALYSIS

Although not required by method 6010B, the serial dilution analysis (five-fold dilution) is performed to evaluate whether significant chemical and physical interferences are present due to sample matrix. The serial dilution analysis must agree within a 10% difference of the original determination after correction for dilution.
Note: Serial dilutions are only required for initial concentrations ≥50 times the IDL for ICP analysis.

8.1 Was a serial dilution performed for each sample matrix for each group of samples as required?
ACTION: If no, note in the data validation report.

8.2 Was field blank used?
ACTION: Note in the data validation report.

8.3 Are results outside of control limits; was a positive or negative interference exhibited?
ACTION: Qualify associated sample results in the same group and matrix as approximate (UJ,J) regardless of whether a positive or negative interference was exhibited.

If more than one serial dilution is performed and exceeds criteria, all associated sample results are qualified.

8.4 List serial dilution analyses and samples qualified due to serial dilution excursions.

Unique Serial Dilution ID	Analyte	%Difference	Action	Samples Affected (client/lab ID)

9.0 FIELD DUPLICATE

Field duplicates, which are blind field samples submitted to the laboratory for analysis, demonstrate sample collection precision. Precision is than evaluated by calculating RPD between the two results.

9.1 Was a field duplicate collected and analyzed according to the QAPP?
Action: If no for the previous question, note in the data validation report that field precision was not evaluated.
9.2 Was the RPD within control limits? For field duplicates consult the QAPP. For field duplicates; a control limit of 20% applies to metals, otherwise laboratory control limits are used. If any result is less than 5 times the reporting limit, a control limit of ± the reporting limit is used to evaluate the result.
Action: Qualify associated sample results of the same matrix as approximate (UJ,J).

9.3 Summarize below samples qualified due to field duplicate excursions.

Field Duplicate ID	Analyte	Excursion	Actions	Samples Affected (client/lab ID)